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31 January 2018

Version of attached file:

Accepted Version

Peer-review status of attached file:

Peer-reviewed

Citation for published item:

Brodie, Mark W. and Aplin, Andrew C. and Hart, Bruce and Orland, Ian J. and Valley, John W. and Boyce, Adrian J. (2018) 'Oxygen isotope microanalysis by secondary ion mass spectrometry suggests continuous 300-million-year history of calcite cementation and dolomitization in the Devonian Bakken Formation.', *Journal of sedimentary research.*, 88 (1). pp. 91-104.

Further information on publisher's website:

<https://doi.org/10.2110/jsr.2018.1>

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**Running Title: CALCITE & DOLOMITE DIAGENESIS IN BAKKEN SANDS USING SIMS O
ISOTOPE MICROANALYSIS**

**OXYGEN ISOTOPE MICROANALYSIS BY SECONDARY ION MASS SPECTROMETRY SUGGESTS
CONTINUOUS 300-MILLION-YEAR HISTORY OF CALCITE CEMENTATION AND
DOLOMITIZATION IN THE DEVONIAN BAKKEN FORMATION**

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Keywords: Diagenesis, Calcite, Dolomitization, SIMS, Oxygen Isotopes

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ABSTRACT

23 Calcite cementation and dolomitization are key diagenetic processes in many sedimentary
24 systems. Unravelling detailed histories and timescales of cementation and replacement is,
25 however, often compromised by the limited spatial resolution of many analytical
26 techniques; in some cases multiple grains are co-analyzed so that diagenetic histories are
27 blurred and reaction periods are difficult to establish. In this study we have used 10-
28 micrometer-resolution, *in situ* secondary ion mass spectrometry to determine the oxygen
29 isotope composition of 197 individual, 10-50-micrometer-size crystals of dolomite and
30 calcite from six samples in a single core of Upper Devonian Middle Bakken Member
31 siltstones and sandstones, the major tight oil formation of the Williston Basin, USA. This
32 amount of data places important constraints on the range of temperatures and times that
33 carbonate cementation and replacement occurred. Petrographic data show that
34 microcrystalline calcite cement is an early phase, and combined with mineralogical data
35 suggest that much of the dolomite replaces calcite. Over spatial scales of less than a
36 centimeter, analyses of individual calcite crystals have a range of 5‰ for $\delta^{18}\text{O}$ in the group
37 of crystals, and for the group of individual dolomite crystals, 10‰. These sub-centimeter
38 ranges are as great as those observed in previous studies of carbonate cements sampled
39 over many meters and remind us that previous low-resolution studies may have
40 inadvertently analyzed mixed phases. There is no relationship between dolomite texture
41 and isotopic composition at this spatial scale; microscale backscattered electron imagery
42 and scanning electron microscopy cathodoluminescence zoning is seen, but cannot be
43 resolved with a 10 micrometer spot size. Assuming, since it is an early cement, that calcite

44 precipitated from seawater ($\delta^{18}\text{O} = -1.5\text{‰}$), it formed at *ca.* 15-40°C, mainly at the lower
45 temperatures. Present-day formation waters in Devonian rocks in this region have oxygen
46 isotope compositions of 7-8‰ VSMOW. Using these values as a likely dolomitizing fluid, we
47 suggest that dolomitization occurred continuously between 40 and 140°C over 150 – 200
48 million years, most likely in a fluid with a high Mg/Ca ratio resulting from gypsum formation
49 in local evaporites. We suggest that this exceptionally low rate of dolomitization was
50 controlled by the low rate of supply of Mg in a very sluggish flow regime; dolomitization is
51 incomplete because of a limited supply of Mg.

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INTRODUCTION

Burial diagenesis transforms sediments into sedimentary rocks through a range of mechanical and chemical processes driven by changes in effective stress and the requirement that mineral assemblages attempt to achieve thermodynamic equilibrium as a function of temperature, pressure, and fluid composition (e.g., Bjørlykke 2014). Although the chemical diagenetic reactions are wide-ranging, depending for example on initial mineralogy and fluid chemistry, questions which are generic to all processes involve (a) the rate of reactions, (b) the extent to which a pre-defined “system” (for example a sand body) is chemically open or closed, and (c) whether or not the reactions occurred continuously or were punctuated (e.g., Giles 1997; Burley et al. 1989; Giles et al. 2000; Gluyas and Coleman 1992; Robinson and Gluyas 1992; Taylor et al. 2010; Bjørlykke and Jahren 2012; Bjørlykke 2014).

These fundamental questions continue to be asked, in part at least, because of limitations in the analytical techniques available to answer them. Many studies have used some combination of petrography, fluid inclusions, and stable isotopes to evaluate diagenetic histories (e.g. Haszeldine et al. 1984; Land et al. 1987; Glasmann et al. 1989; Brint et al. 1991; Aplin and Warren 1994; Williams et al. 1997; Sullivan et al. 1997; Taylor et al. 2000; Girard et al. 2001; Goldstein 2001; Marchand et al. 2002; Schmid et al. 2004). However, diagenetic silicate and carbonate minerals in sandstones commonly form grains or overgrowths on scales less than 100 micrometers and may have grown over many millions of years. Detailing growth histories of individual phases thus requires probes which can operate on a sub-10-micrometer scale. Conventional stable-isotope and fluid-inclusion studies cannot unravel these histories because (a) the resolution of isotopic analyses is

76 insufficient and (b) fluid inclusions tend to occur in specific locations of diagenetic phases,
77 for example at grain-overgrowth boundaries or in healed microfractures (e.g., Osborne and
78 Haszeldine 1993).

79 Oxygen isotopes preserve important information about the temperature at which minerals
80 form and the nature of the fluids from which they precipitate. Earlier isotopic studies on
81 diagenetic quartz and carbonate were made on whole overgrowths or areas sampled with
82 microdrills, and could not generate temporal data (Lee and Savin 1985; Land et al. 1987;
83 Brint et al. 1991; Hart et al. 1992; Macaulay et al. 1993; Aplin and Warren 1994; Taylor et al.
84 2000; McBride and Milliken 2006). *In situ* isotope studies on well-identified minerals can
85 overcome uncertainties of what is being analyzed, but neither the resolution (20–30 μm)
86 nor the precision ($\pm 2\text{‰}$; 2SD) of earlier work using single-collector secondary ion mass
87 spectrometers (SIMS) were sufficient to constrain growth histories (Graham et al. 1996;
88 Williams et al. 1997; Lyon et al. 2000; Girard et al. 2001; Marchand et al. 2002). Technical
89 advances in SIMS now allow *in situ* analyses to be made on 2–10- μm -diameter regions and
90 have revealed up to 10‰ ranges in $\delta^{18}\text{O}$ in single quartz overgrowths and carbonate
91 cements (Pollington et al. 2011; Harwood et al. 2013; Śliwiński et al. 2016b).

92 Carbonates are common and often pervasive cements in marine sandstones (e.g. Bjørkum
93 and Walderhaug 1990, 1993; Macaulay et al. 1993; Klein et al. 1999; Taylor et al. 2000;
94 McBride and Milliken 2006). Although significant carbonate cement can be formed during
95 early burial (e.g., Bjørkum and Walderhaug 1990; 1993), oxygen and carbon isotope data
96 often show a wide range of values which imply a range of precipitation temperatures and/or
97 fluid compositions (e.g., Klein et al. 1999; Taylor et al. 2000). However, detailed
98 petrography, for example using backscattered electron microscopy, commonly reveals

chemically distinct carbonate phases on a sub-millimeter scale (e.g., Hart et al. 1992; Taylor et al. 2000; Śliwiński et al. 2016b). This means that conventional isotope analyses, in which areas of at least a few millimeters are sampled, are likely to result in the analysis of mixed phases or of a single phase that has grown over a long period of time. Equally, studies which have used selective leaching to isolate compositionally distinct carbonate phases rely on the specificity of the leaching method (e.g., Macaulay et al. 1993; Klein et al. 1999). The nature of these analytical tools means that diagenetic histories are inevitably blurred or uncertain.

Dolomite and calcite grains examined in this study of the Upper Devonian Middle Bakken Member in North Dakota are often smaller than 100 micrometers. The use of high-resolution SIMS, an analytical tool which allows oxygen isotope data to be collected from areas 10 micrometers in diameter, is thus essential if the timing and evolution of fluids responsible for the formation of these diagenetic phases are to be unravelled accurately. The Bakken Formation has recently received much attention as a highly significant unconventional hydrocarbon accumulation, and the occurrence of both calcite and dolomite is central to the quality of the petroleum reservoir (e.g., Li et al. 2015). Previous work on the oxygen-isotope composition of carbonates in the Bakken has been limited to studies of calcite in fracture fills (Pitman et al. 2001), the bulk analysis of mixed carbonates (Karasinski 2006), and one grain-scale study (Staruiala et al. 2013). Here, we report oxygen isotope data obtained by SIMS on calcite and dolomite grains and focus on four questions: (a) over what temperature and period of time did the carbonate phases form; (b) was carbonate diagenesis continuous or punctuated; (c) is the dolomite a primary cement or did it form through dolomitization of earlier calcite (e.g., Warren 2000; Machel 2004); and (d) to what extent did diagenesis occur in a closed or open geochemical system?

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GEOLOGICAL CONTEXT

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The Upper Devonian-Lower Mississippian Bakken Formation was deposited over wide areas of the intracratonic Williston basin, which covers 770,000 km² of Montana, North Dakota, and South Dakota in the USA and parts of Saskatchewan and Manitoba in Canada (Fig. 1).

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The basin is structurally simple with an almost complete stratigraphic section and only gentle, low-wavelength folding (Webster 1984; Meissner 1991). The burial history, based on a well which has a stratigraphy very similar to that of the core used in this study and in which the Bakken is buried to essentially the same depth, is one of continual subsidence from deposition to *ca.* 50 Ma, followed by modest uplift and renewed subsidence from 35 Ma to the present day (Kuhn et al. 2012) (Fig. 1C). The present-day temperature for the samples of this study is around 125 °C with a modelled maximum temperature between 150 and 160 °C.

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The Bakken is divided into three stratigraphic members (Fig. 2). The Upper and Lower members are both organic-rich shales whilst the Middle Bakken Member, the subject of this study, comprises a variably but often highly carbonate-cemented series of very fine-grained sandstones and siltstones deposited over large areas of a shallow, epicontinental sea (Meissner 1978; Freisatz 1995; Egenhoff et al. 2011). At the depocenter of the Williston Basin the Middle Bakken reaches a maximum thickness of 46 m but varies in thickness across the basin (Pitman et al. 2001). Most current work suggests that the Middle Bakken was deposited in a variety of shallow-marine environments during a Late Devonian to Early Mississippian regression (e.g., Li et al., 2015). Whilst the sedimentology of the Middle Bakken has been extensively described (McCabe 1959; Meissner 1978; Webster 1984;

Holland et al. 1987; Smith and Bustin 1996; Pitman et al. 2001; Egenhoff et al. 2011; Egenhoff 2017), diagenetic studies are more limited. Nevertheless, pervasive early calcite cement has been recognized in several studies (Last and Edwards 1991; Pitman et al. 2001; Ferdous 2001; Li et al. 2015), along with the interpretation of several phases of dolomite (Ferdous 2001).

EXPERIMENTAL METHODS

Samples

Samples for this study come from a single core drilled in McKenzie County, North Dakota, USA (Fig. 1B). The core was described using the five facies associations defined by Simenson (2010) in a study of the Middle Bakken from the Parshall Field, Mountrail County, North Dakota. A total of 32 core plugs were taken over the full thickness of the Middle Bakken section; 6 of the 32 samples were selected for this study, including samples from each of the five different facies.

Petrography

Thin sections were cut perpendicular to bedding from core plugs and carbonate textures investigated using both transmitted-light and electron microscopy. Transmitted-light microscopy was carried out using a Nikon Eclipse 50iPOL polarizing microscope. 300 points per sample were counted using a Petrolight petrographic point counter. The thin sections were then coated with a 30 nm layer of carbon before analysis by electron microscopy.

Electron microscopy was performed at Durham University's GJ Russell Electron Microscopy Facility on a Hitachi SU 70 FEG SEM in secondary (SE) and backscatter (BSE) and Cathodoluminescence (CL) modes. Images were acquired at 15 kV, 2-4 nA and a working distance of 15-16 mm.

Dolomite crystal textures were classified using the scheme described by Sibley and Gregg (1987). Whilst proposed principally for dolomite crystals in carbonate rocks, this scheme is also appropriate for low-temperature, mixed clastic-carbonate systems like the Bakken because it focuses on the grain-boundary and grain-size relationships of individual crystals, which can be used to infer the genetic origin of each dolomite crystal class.

Scanning Electron Microscopy - Cathodoluminescence (SEM-CL) images were acquired on carbon-coated thin sections and round resin plugs using the Hitachi SU 70 FEG SEM with a Gatan Mono-CL detector operated in panchromatic mode. Images were obtained at an accelerating voltage of 10 kV and a working distance of 17 mm. Spectral information was obtained over a wavelength search range of 505 - 800 nm and a dwell time of approximately 3,200 μ s per pixel for an image resolution of 2250 x 2250. Intensity values were corrected using the system response curve.

Using SEM-WDS, the elemental compositions of 58 calcite crystals and 155 dolomite crystals with different textures in 13 samples were determined, including the six samples on which SIMS analyses were performed. Analyses were repeated three times per crystal, and the results for each crystal are reported as the mean of the three analyses.

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Mineralogy

189 Bulk mineralogy was determined by KT Geoservices (Table 1). X-ray diffraction (XRD)
190 analysis was conducted using a Siemens D500 automated powder diffractometer equipped
191 with a copper X-ray source (40 kV, 30 mA) and a scintillation X-ray detector. Both bulk and
192 clay (< 4 µm) analyses were conducted. Quantitative data were obtained from the whole-
193 rock pattern using whole pattern fitting (WPF) and Rietveld refinement methods.

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Bulk C and O Isotope Analysis

196 The carbon and oxygen stable-isotope composition of bulk calcite and dolomite were
197 analyzed at the Scottish Universities Environmental Research Centre (SUERC) on an
198 Analytical Precision AP2003 mass spectrometer equipped with a separate acid injector
199 system (Table 1). We attempted to separate calcite and dolomite through the preferential
200 dissolution of calcite by reaction with 105% H₃PO₄ under a helium atmosphere at 70 °C. As
201 shown later, our results in fact indicate that the fine-grained dolomite in these samples was
202 also substantially dissolved with this method. Measured O isotope ratios are reported as per
203 mil deviations relative to Vienna standard mean ocean water (VSMOW) and C isotopes
204 relative to Vienna PeeDee Belemnite (VPDB) using conventional delta (δ) notation. Mean
205 analytical reproducibility based on replicates of the SUERC laboratory standard MAB-2
206 (Carrara Marble) was around ± 0.2‰ for both carbon and oxygen. MAB-2 is an internal
207 SUERC laboratory standard extracted from the same Carrara Marble quarry as the IAEA-CO-
208 1 international standard. It is calibrated against IAEA-CO-1 and NBS-19 and has exactly the
209 same C and O isotope values as IAEA-CO-1 (-2.5‰ and 2.4‰ VPDB respectively).

210

211

Secondary Ion Mass Spectrometry

212 *In-situ*, sub-grain-scale oxygen stable-isotope data were obtained using secondary ion mass
213 spectrometry. Based on their mineralogy and petrographic characteristics, six
214 representative samples were selected, one from each facies. Soluble organic matter was
215 removed using a standard, 96 hour soxhlet extraction procedure using a mixture of
216 dichloromethane and methanol. The samples were then mounted in epoxy resin in 1-inch
217 round plugs. Several crystals (2 or 3) of calcite standard UWC-3 ($\delta^{18}\text{O}_{\text{VSMOW}}$ of UWC-3 is
218 $12.49\text{‰} \pm 0.03\text{‰}$ 1 SD, $n = 9$; Kozdon et al. 2009) were mounted at the center of each
219 sample. The sample was then polished sequentially with 6 μm , 3 μm , and 1 μm diamond
220 paste on a low-nap pad. The final polish was obtained using a 0.05 μm colloidal alumina
221 solution on a vibrating pad for 30-200 seconds. The polished sample plugs were then gently
222 cleaned with deionized water and ethanol, and dried in a vacuum oven for 5 hours at 40°C.
223 To prevent charging during analysis, samples were coated with 60 nm gold. The flatness
224 across the samples was measured using a white-light profilometer across both the polished
225 rock, the mounted and polished calcite standard, and enclosing epoxy. The maximum
226 topography recorded was 3 μm (sample) and 7 μm (sample and standard). Analysis spots
227 were not placed near localized areas with relief $> 3 \mu\text{m}$.

228 *In-situ* oxygen isotope data were acquired using a CAMECA IMS 1280 large-radius multi-
229 collector ion microprobe at the WiscSIMS Laboratory at the University of Wisconsin-
230 Madison (Kita et al. 2009; Valley and Kita 2009). A $^{133}\text{Cs}^+$ primary ion beam with a current of
231 1.4 nA was focused at the analytical surface, resulting in ellipsoidal pits ca. 10 μm x 13 μm in

size. The typical secondary $^{16}\text{O}^-$ ion intensity for the 300 analyses of this study was approximately 2.5×10^9 cps.

Both before and after every set of 8-17 sample analyses, a sample-mounted calcite standard (UWC-3) was measured four times. As for conventional analyses, stable-isotope ratios are reported using the standard delta notation relative to VSMOW ($\delta^{18}\text{O}$ ‰). The reproducibility of each set of unknown samples is reported as 2 SD of the bracketing standard analyses; the average 2 SD of bracketed analyses was 0.27‰ (refer also to the supplementary material). Detailed analytical protocols can be found in Kita et al. (2009).

Initial SEM-EDX observations indicated the presence of iron in some of the dolomite crystals. Śliwiński et al. (2016a) show that the extent of isotopic fractionation occurring during SIMS analysis of carbonates (matrix effect) is a function of the concentration of iron. Thus, instrument standards for the dolomite – ankerite series were analyzed during the same SIMS session to ensure the accuracy and precision of analyses for the full range of potential carbonate chemistries. In addition, the carbonate in each pit analysed by SIMS was identified in the SEM, and the iron composition of the crystal measured using SEM-WDS (adjacent to the pit), using an INCA Wave 700 spectrometer WDS detector attached to a Hitachi SU-70 FEG SEM. The SEM “spot size” (beam diameter) was between 1.7 and 5 nm with an interaction depth of up to 800 nm and width of around 3 μm . To ensure that the analyses were of specific crystals, only crystals with the shortest visible length of > 2 μm were analysed. Three sets of standards were used for SEM-WDS: (a) an elemental cobalt instrument standard was used at the start of every session; (b) at the start and end of each analytical session, the calcite standard UWC-3 (see Kozdon et al. 2009) which was mounted to the center of all of the analyzed samples was measured five times; (c) a series of

carbonate standards with known chemical compositions (calcite, ankerite, dolomite, and siderite) were analyzed to measure accuracy and precision (see Supplementary Material 2). Using the results of SEM-WDS analysis, we used the mass bias calibration method proposed by Śliwiński et al. (2016a) to correct SIMS $\delta^{18}\text{O}$ measurements for the presence of iron in the dolomite crystals (Supplementary Material). Only 8 analyses required correction for the presence of iron, since iron contents were generally less than the detection limit of 0.1 wt. % FeO. The residual of the dolomite-ankerite calibration curve, fitted through seven standard materials measured during the same SIMS session, was 0.25‰.

RESULTS

Sedimentology, Mineralogy and Petrography

The Middle Bakken is a sedimentologically heterogeneous fine sandstone - siltstone unit that is pervasively but variably cemented by both calcite and dolomite. Using the framework provided by Simonsen (2010) and the sedimentologic description of this core by Li et al. (2015), five facies (B, C, D1, D2, and E) were defined from the base (3206 m) to the top (3182 m) of the core, with a gradational facies between B and C. Facies B comprises strongly bioturbated, argillaceous, calcareous sandstones and siltstones; facies C consists of very fine-grained sandstones and siltstones showing both planar and undulose lamination, with some thin mud-rich horizons; facies D1 is a fine-grained sandstone with common soft-sediment deformation features; facies D2 consists of a light brown to light gray, parallel to undulating-laminated, low-angle cross-laminated sandstone; facies E comprises a dark gray

276 siltstone interbedded with a light gray, thinly parallel-laminated, very fine-grained
277 sandstone.

278 Core photographs taken with both white and UV light (Fig. 3) suggest that in all facies, there
279 are multiple 2-30 cm-thick zones of layered or nodular diagenetic carbonate where porosity
280 has been infilled to the extent that they do not contain fluorescing oil (i.e., calcite
281 cementation pre-dated oil migration; Li et al. 2015). Other areas, which do contain
282 fluorescing oil, are more lightly and/or more variably carbonate-cemented. Based both on
283 the XRD analysis of 13 samples and point counting of 15 samples, calcite (both primary,
284 bioclastic calcite and diagenetic calcite) constitutes 3-56% of the rock volume and diagenetic
285 dolomite between 5 and 41% (Table 1). Total carbonate content (calcite plus dolomite,
286 including bioclastic calcite) varies between 32 and 72%. The average minus-cement porosity
287 is 42% (range 36-46%), close to depositional porosity, and suggesting that cementation
288 started close to the sediment-water interface. The inverse correlation between the amounts
289 of calcite and dolomite ($r^2 = 0.62$) lends support to the idea that dolomite is replacing calcite
290 rather than being a primary cement.

291 At the core scale, calcite- and dolomite-cemented regions are present in approximately 70%
292 of the core. In thin section, diagenetic calcite and dolomite cement occurs as bands. These
293 bands vary in thickness from a couple of millimeters up to the size of the full section. Whilst
294 in most instances the millimeter-scale bands form sharp contacts parallel to bedding, in
295 some cases there is no clear lithological control on the morphology of the contact or the
296 spatial distribution within the section.

297 Diagenetic calcite is observed in two textural types. By far the most volumetrically
298 important texture (Type 1) is pervasive, poikilotopic cement in which detrital grains “float”

299 within the calcite (Figs. 4D and 5A). Similar, early, massive calcite cement is common in
300 shallow-marine sandstones (e.g., Bjørkum and Walderhaug 1993). Type 2 calcite comprises
301 individual crystals which (a) appear to cement small numbers of grains to form a globular
302 morphology (Fig. 5B), and (b) occur as individual, discrete grains which do not connect other
303 grains; visual estimates from SEM show that these phases form < 1% of calcite.

304 Dolomite occurs as six different morphologies. Type 1 dolomites are nonplanar, anhedral,
305 crystals with rounded edges, 15-30 μm in size (Fig. 6A). Type 2 dolomites are euhedral
306 rhombs, 10-50 μm in size with micrometer-scale pores in their core (Fig. 6B). Type 3
307 dolomites are euhedral rhombs, 10-50 μm in size but without pores (Fig. 6C). Type 4
308 dolomites are subhedral, geometric, angular crystals which vary in size from 5 to 35 μm (Fig.
309 6D). Type 5 dolomites are 2-10- μm -thick ferroan rims which form around more
310 stoichiometric, iron-poor dolomite. This phase has been observed around all other dolomite
311 types (Fig. 6E). Type 6 dolomites are euhedral rhombs which are less than 5 μm in diameter
312 (Fig. 6F). Under transmitted light, some dolomites show a “cloudy core” texture which has
313 been previously suggested to result from the dolomitization of a calcite precursor, resulting
314 in a close-to-stoichiometric dolomititic outer zone and a more calcium-rich and porous core
315 (Murray and Lucia 1967; Sibley 1982).

316 In most cases, except in the relatively unusual cases of Fe enrichment towards the edge of
317 crystals, BSEM shows no evidence of significant changes in the chemical composition of
318 dolomite crystals from core to edge. Scanning electron microscopy - cathodoluminescence
319 (SEM-CL) does however reveal zoning within individual dolomite crystals. Zones of different
320 luminescence can reflect both subtle changes in crystal chemistry and/or variations in
321 growth mechanisms (e.g. Boggs and Krinsley 2006), and our data are insufficient to

determine the reasons for the zonation. In total, 48 crystals were viewed in 10 samples. The CL character of individual dolomite types was consistent in all the samples and is reported in Figure 7. All dolomite phases luminesce in the red part of the spectrum, including the “dull” zones which simply have a lower - intensity luminescence (Fig. 7). Anhedral, Type 1 dolomites show incomplete concentric zones which have decreasing luminescence intensity towards the edge of the crystals. Textural types 2-4 and 6 exhibit similar CL characteristics: a single, concentric, low - intensity luminescence zone around a much more intensely luminescing core. The rims are approximately 1-10 μm in thickness (Fig. 6E). Type 5 dolomites are ferroan rims which form single homogeneous layers around other dolomite crystals; they show low emission intensity in the red spectrum.

Chemical Composition

Calcite cement has a very consistent chemistry, averaging 97.4 mol % Ca, 2.4 mol % Mg, and 0.2 mol % Fe (Fig. 8). Eighty percent of dolomite analyses have chemical compositions between $\text{Ca}_{0.55}\text{Mg}_{0.45}\text{CO}_3$ and $\text{Ca}_{0.45}\text{Mg}_{0.55}\text{CO}_3$, with a modal value close to that of stoichiometric dolomite. There is no obvious relation between dolomite composition and textural type (Fig. 8). Almost all dolomites have low iron contents, with 85% containing less than 2 mol % Fe and only 2 % with more than 6 mol % Fe. Note however that because of their spatial scale, Type 5 dolomites (ferroan dolomite rims) were not systematically measured, although they quite commonly form either as discrete rims or more diffuse alteration zones around all other textural types of dolomite; they also form small, individual crystals with anhedral to euhedral habits.

Diagenetic dolomite containing more than 55 mol % Mg are uncommon in the literature; however, in this study, 17% of the analyses are more Mg-rich than $\text{Ca}_{0.45}\text{Mg}_{0.55}\text{CO}_3$. Most of these analyses are from Samples 2 and 4, and the most common chemistry is around $\text{Ca}_{0.4}\text{Mg}_{0.6}\text{CO}_3$, i.e., between the composition of stoichiometric dolomite ($\text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3$) and huntite ($\text{Ca}_{0.25}\text{Mg}_{0.75}\text{CO}_3$).

Bulk C and O Isotope Composition

The results of bulk carbon and oxygen isotope analyses are reported in Table 1. The ranges for putative calcite and dolomite overlap substantially and are approximately -3 to +3‰ for carbon and +20 to +30 ‰ for oxygen (putative dolomite) and +22 to +26‰ (putative calcite). We use “putative” because with the benefit of the SIMS oxygen isotope analyses of individual calcite and dolomite crystals (see below) it is clear that the selective leach partially dissolved dolomite as well as calcite. This is readily understood, as, in practice, the “calcite” fraction is that gas extracted from the bulk samples after three hours of acid digestion in a vacuum; the “dolomite” fraction is the gas then extracted after a further 24-hour acid digestion on the residue (both corrected back to original carbonate as true calcite or dolomite). Whilst such “dolomite” analyses are likely to be free of calcite, the “calcite” is susceptible to contamination, as is shown by this study. Retrospectively, the advice is to proceed with caution when interpreting previous studies, which have used similar selective leaching techniques in an attempt to separate finely intergrown calcite and dolomite, particularly with the “calcite” data.

The main result of the bulk isotope analyses is that most of the carbon in both dolomite and (probably) calcite is from marine carbonate, with only minor inputs from organic sources. Values between -3‰ and +3‰ suggest the addition of relatively small amounts of organic carbon from processes involving coupled methanogenesis and CO₂ reduction, which would result in more positive values, and from the oxidation of organic matter, which would result in more negative values (e.g., Curtis et al. 1986).

SIMS: Grain-Scale Oxygen Isotope Data

Three hundred and eight sites were analyzed from the six samples selected for SIMS analysis. After analysis, SEM was used to examine the shape of the pits formed by the ion beam. Previous work (Cavosie et al. 2005; Linzmeier et al. 2016) has shown that data from morphologically irregular pits are less reliable than those from regularly shaped pits. In this study we took a very strict approach to ensure that only the most reliable data were included. Some data were rejected due to the very fine nature of these samples, such that some mixed phases were measured. Most of the rejected data are in fact from crystals with minor irregularities such as surface asperities. All rejected data are reported in the Supplementary Material. Using these strict criteria, we accepted 197 analyses, i.e., between 16 and 46 analyses from six sample areas, each of which is approximately 5 mm in diameter. Values of $\delta^{18}\text{O}$ for individual calcite grains are almost all between +28.9 and +33.7‰ (-1.9 – 2.8 ‰ VPDB), with a similar range in samples from each facies (Fig. 9). For dolomite, the full range is +22.5 – 32.2‰ (-8.1 – 1.3 ‰ VPDB), with a mean value of +26.8‰ and with 93% of values between +24 and +30‰ (Fig. 9). There is a similar range of $\delta^{18}\text{O}$ values in each

morphological type of dolomite. There is no relation between $\delta^{18}\text{O}$ and the Ca/Mg ratio of dolomite.

DISCUSSION

The oxygen isotope data in this study show as great a range on a sub-centimeter scale as many studies have found on conventional studies of diagenetic carbonates in sandstones sampled on scales of many meters (e.g., Bjørkum and Walderhaug 1993; Klein et al. 1999; Taylor et al. 2000). Given the sub-millimeter complexity observed in this study (Fig. 10), it is clear that conventional sampling methods can easily homogenize complex mixtures and result in an enforced, simplistic picture of diagenetic histories. Equally, however, our results show an overall commonality from sample to sample which show that carbonate diagenesis, although complex on a sample scale, proceeded in a similar way throughout fifteen meters of the Middle Bakken. With SIMS, the large number of analyses of accurately identified mineral phases allows us to draw a temporal picture of diagenesis which is not possible with conventional data. As we discuss below, our data suggest that carbonate diagenesis in the Middle Bakken was not episodic but occurred continuously over an approximately 300-million-year period of burial.

High minus-cement porosities suggest that diagenetic calcite started to precipitate close to the sediment-water interface, as observed in many similar studies (e.g., Wilkinson 1991; Gluyas and Coleman 1992; Bjørkum and Walderhaug 1990; 1993; Taylor et al. 2000). Our isotopic data support the early formation of calcite. Using the isotope paleothermometer proposed by O'Neil et al. (1969) for calcite and assuming a $\delta^{18}\text{O}$ of = -1.5‰ for Late

409 Devonian seawater (Hudson and Anderson 1989; van Geldern et al. 2006), the vast bulk of
410 calcite formed between 15 and 35 °C (Fig. 11).

411 The temperature histogram in Figure 11A suggests that the bulk of calcite cementation
412 occurred between 15 and 20 °C with steadily decreasing amounts at higher temperatures.
413 Assuming a mean seawater temperature of 15 °C, a geothermal gradient of 25 °C/km, and
414 an unchanging $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, calcite cementation occurred at decreasing rates during burial to *ca.*
415 800 meters. Linking this to the burial history (Fig. 1), calcite cementation occurred over the
416 first *ca.* 10 million years of burial. Given the occurrence of bioclasts in the Middle Bakken
417 and the carbon isotope signature of calcite ($0 \pm 3\text{‰}$), this calcite most likely represents the
418 redistribution of biogenic calcite via local dissolution and precipitation.

419 Petrographic observations of (a) cloudy cores (transmitted light) and (b) porosity which
420 likely results from the volume reduction associated with the replacement of calcite by
421 dolomite (Weyl, 1960), combined with (c) the inverse correlation between the amounts of
422 dolomite and calcite, suggest that dolomite is largely replacing calcite rather than occurring
423 as a pore-filling cement. In the absence of reaction fronts in individual crystals, it appears
424 that dolomitization is a dissolution – precipitation reaction in which calcite is dissolved and 5
425 – 50-micrometer-size dolomite crystals are precipitated. The carbon isotope data for
426 dolomite and calcite-dolomite mixtures are similar and are thus also consistent with
427 dolomitization of calcite. Using the oxygen isotope paleothermometer proposed for
428 dolomite by Vasconcelos et al. (2005) for dolomite-water and assuming, as a first estimate,
429 that dolomite formed in unmodified seawater ($\delta^{18}\text{O}_{\text{H}_2\text{O}} = -1.5\text{‰}$), a temperature range of 13
430 - 66°C is calculated (Fig. 11B). Based on a correlation between $\delta^{18}\text{O}$ and the Ca content of
431 diagenetic dolomites, Vahrenkamp et al. (1994) suggested that when estimating

precipitation temperatures for dolomite, a correction of +0.1 per mil may be needed per mol % of Mg deficiency due to variations in mineral-water isotope fractionation factors. For most of our data, this results in a correction of only < 0.3‰, with a maximum correction of 1.5‰; the range of estimated precipitation temperatures remains unchanged.

Since dolomite is supersaturated in seawater, dolomitization in unmodified seawater is geochemically feasible, but unusual (e.g., Machel 2004). Dolomitization more commonly occurs in fluids in which the Mg/Ca ratio has been modified as a result of evaporation and precipitation of gypsum (e.g., Budd 1997; Warren 2000; Machel 2004 for reviews).

Anhydrite-bearing evaporites occur both below (Devonian Prairie Evaporite and Three Forks formations) and above (Mississippian Charles Salt Formation) the Bakken Formation, and pre-Mississippian waters in this part of the Williston Basin are commonly hypersaline and are likely dolomitizing fluids (Iampen and Rostron 2000). Values of $\delta^{18}\text{O}$ for present-day formation waters from the Devonian Duperow aquifer, which occurs below the Bakken in this part of the Williston Basin, are around +7.5 ‰ (Figure 1A; Rostron and Holmden 2003).

If we assume a value of +7.5‰, the maximum calculated precipitation temperature is 157 °C, approximately that of the maximum burial temperature (Fig. 11D). If all dolomite formed from water with $\delta^{18}\text{O} = +7.5\text{‰}$, then precipitation temperatures range from 61 to 157 °C (Fig. 11D). Slightly lower $\delta^{18}\text{O}$ values, for example +7‰, would give a temperature range of 58 – 150 °C. The histogram of estimated precipitation temperatures shows that the rate of dolomitization increases steadily from 60 to 130 °C and then decreases at higher temperatures (Figure 11D). Given that dolomitization rates increase with temperature, the limited reaction at the highest temperatures might reflect the generation of petroleum from the organic-rich shales above and below the middle Bakken and its emplacement into the

455 middle Bakken. If we assume that dolomitization occurred in fluids that evolved steadily
456 from the original seawater (-1.5‰) to the present-day brine (+7.5‰), then dolomite would
457 have formed throughout almost the whole burial history of the Bakken (Figs. 1, 11). In either
458 case, dolomitization occurred continuously over approximately 150 – 250 million years.

459 The rate of dolomitization depends on a range of factors, including the Mg:Ca ratio in
460 solution (Kaczmarek and Sibley 2007), the mineralogy of the reactant (Gaines 1974), and
461 reactant surface area (Sibley et al. 1987). Rate constants for dolomite precipitation have
462 been measured experimentally (Arvidson and Mackenzie 1999), and even at low diagenetic
463 temperatures the resulting kinetics show that pervasive dolomitization and dolomite
464 precipitation can occur on timescales of less than one million years (Whitaker and Xiao
465 2010; Al Helal et al. 2012); this is consistent with the occurrence of Holocene dolomites in
466 modern sabkhas and carbonate islands (Budd 1997). Dolomitization rates increase markedly
467 with increasing temperature (Arvidson and Mackenzie 1999) so that at the estimated
468 temperatures of dolomitization in the Bakken (61 – 157 °C), rates are not controlled by
469 kinetics. Rather, we suggest that the rate of dolomitization must be limited by the rate at
470 which Mg is delivered to reaction sites and thus the fluid flow regime (Machel 2004;
471 Whitaker et al. 2004). We have no way of evaluating the detailed flow history through the
472 Bakken in North Dakota, but the highly saline and isotopically evolved waters which occur in
473 the region today are likely to be part of an ancient, highly restricted and almost stagnant
474 flow system (Rostron and Holmden 2003). With no topographic recharge in the area, fluid
475 flow would be driven almost entirely by sediment compaction, with very low water:rock
476 ratios. The lack of fluid flow and related supply of Mg is the most likely reason why

dolomitization, despite the length of time available for reaction, is partial rather than complete.

As in almost all diagenetic studies, the lack of constraint of paleo- $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ limits our ability to generate highly constrained diagenetic time-temperature histories. In principle, clumped-isotope studies will allow this because precipitation temperatures can be fixed without the need to assume $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (Dale et al. 2014; Millán et al. 2016). However, the sample sizes currently required for clumped-isotope work precludes the grain-scale analyses such as those reported here. For the finely intergrown dolomites and calcites analyzed in this study, clumped isotopes would have yielded a range of temperatures depending on the mixture of calcite and dolomite grains drilled from each sample.

SUMMARY AND CONCLUSIONS

Shallow-marine fine-grained sandstones and siltstones from the Devonian Middle Bakken Member are pervasively cemented with calcite and dolomite. Petrographic and mineralogical data show that dolomite occurs as a result of dolomitization of calcite.

The oxygen isotope composition of 57 individual calcite and 174 individual dolomite grains from six samples were determined using SIMS. A similarly wide range of values occurs in all six samples: 5‰ for calcite and 10‰ for dolomite. For dolomite, there is no relationship between morphology, chemistry, and isotopic composition, so that in this case petrography is not a good guide to diagenetic history.

Since all samples display the same range of oxygen isotope values, we conclude that whilst carbonate diagenesis in the Middle Bakken is heterogeneous on a millimetre scale, the same set of diagenetic processes are occurring on the same timescales on a 20-meter scale. Furthermore, the range of oxygen isotope compositions that occur on a millimeter scale are similar to the total ranges determined in many conventional isotope studies of carbonate-cemented sandstones sampled on scales greater than a meter. It is likely that either mixed phases or isotopically diverse single phases have been analyzed in previous studies, resulting in blurred or incorrect diagenetic histories.

A great benefit of SIMS is that through the generation of a large number of analyses of known phases, a much more accurate diagenetic history can be elucidated compared to conventional studies in which either sample numbers are restricted or there is uncertainty over what phases have been analyzed. In this study we can be confident that carbonate diagenesis has been almost continuous from deposition to maximum burial: a period of 300 million years. Within the uncertainty of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, calcite formed over the first *ca.* 10 Myr of burial, with most forming close to the sediment water interface. Dolomitization occurred continuously from *ca.* 61 – 157 °C over 150 – 250 million years. The rate of dolomitization was probably controlled by the rate of supply of Mg in a very sluggish flow regime; dolomitization is probably incomplete because of a lack of Mg and perhaps, in this case, by the fact that petroleum was emplaced into the sandstone late in the burial history.

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836 **ACKNOWLEDGEMENTS**

837 The authors are grateful to Statoil, who funded this work, and to the team at Wisconsin
838 SIMS Laboratory for their assistance. WiscSIMS is supported by the National Science
839 Foundation (EAR-1355590) and the University of Wisconsin-Madison. Our thanks are
840 extended to the team at Scottish Universities Environmental Research Centre (SUERC) for

841 assistance in obtaining bulk stable-isotope measurements. Thanks are also extended to KT
842 Geoservices for XRD analysis. We thank reviewers Tony Buono and Sven Egenhoff, and AE
843 Joe Macquaker, for their insightful comments, which focused and improved the manuscript.
844 John Southard's editing is also very much appreciated.

845

LIST OF FIGURES

Figure 1 - A) Map of northern USA and southern Canada showing states and provinces. ND – North Dakota. B) Map of North Dakota, showing the location of the well in this study and that modelled in the Kuhn et al. (2012) study. C) Burial history of the Williston Basin developed for the basin center in North Dakota. The temperature through time is overlaid. Cambr - Cambrian, Ordov - Ordovician, Sil - Silurian, Carbon - Carboniferous, Pal - Paleogene, N - Neogene, Up - Upper, Mi - Middle, Lo - Lower, Penn - Pennsylvanian, Mio - Miocene. From Kuhn et al. (2012).

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873

874 **Figure 5** - Backscattered electron micrographs of the various textural types of diagenetic
875 calcite identified in the Middle Bakken Formation. A) Type 1 calcite; forming a pervasive
876 cement; B) Type 2 calcite; forming discrete grains, partially cementing other grains.

877

878 **Figure 6** - Backscattered electron micrographs of the various textural types of dolomite
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884

885

886 **Figure 7** – SEM-CL spectra of the six different dolomite textures: A) Mixed SE-inline BSE image; B)
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889

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894

895 **Figure 9** – A) Grain-scale oxygen isotope data collected by SIMS, differentiated by sample
896 [SIMS sample numbers S2-S7; see Table 1 for details of individual samples]. Calcite and
897 dolomite are separated for comparison. B) Grain-scale oxygen stable-isotope data collected
898 by SIMS for dolomite differentiated by textural types T1-T6 [Refer to Figure 6 for textural
899 types]. Oxygen isotope data are reported relative to VSMOW. Error bars (2 SD) are plotted
900 but are in most cases smaller than the data-point marker.

901

902 **Figure 10** - Secondary electron micrographs showing positions of SIMS analyses. $\delta^{18}\text{O}_{\text{SMOW}}$
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904 calcite (3), sample 2, sites 2-004 (1), 2-013 (2) and 2-081 (3) [Excluded due to a boundary
905 breach]. B) An analysis pit at the center of the dolomite crystal, sample 1, site 1-051. C) four
906 analysis pits; 2-4 were taken in a transect across a crystal of dolomite, sample 1, sites 1-073

907 (1), 1-071 (2), 1-071a (3) and 1-071b (4) [Note that analysis 1 was excluded from the dataset
908 due to a boundary break]. D) Analysis pits from three crystals of dolomite (1) and calcite (2,
909 3 and 4), sample 3, sites 3-033 (1), 3-022 (2), 3-026 (3), 3-021 (4). [Note that analyses 1 and
910 2 were excluded from the data set due to a boundary breaches]. Refer to Table 1 and
911 Supplementary Information for further information on each sample and individual sites.

912

913 **Figure 11** – Histogram of calculated precipitation temperatures from SIMS $\delta^{18}\text{O}$ values for:

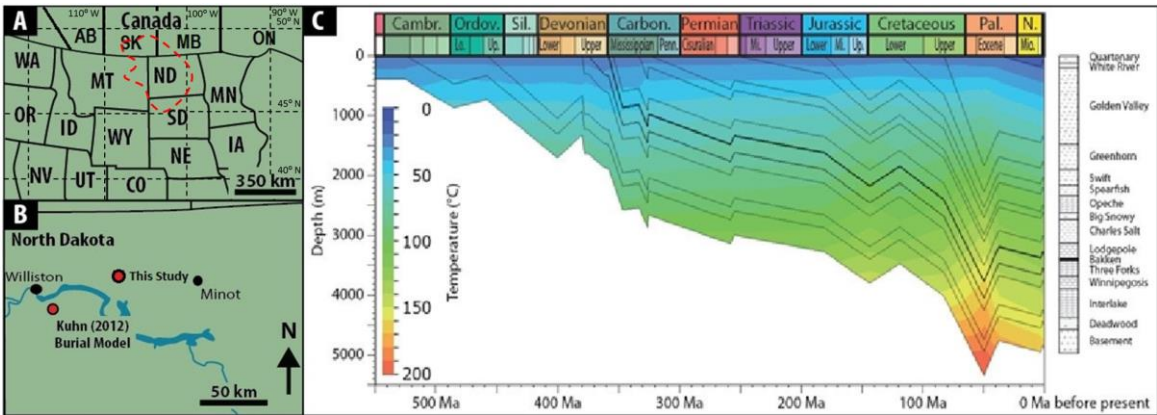
914 A) Calcite, assuming $\delta^{18}\text{O}_{\text{water}} = -1.5\text{‰}$; B) Dolomite, assuming $\delta^{18}\text{O}_{\text{water}} = -1.5\text{‰}$; C)

915 Dolomite, assuming $\delta^{18}\text{O}_{\text{water}} = +3\text{‰}$; D) Dolomite, assuming the $\delta^{18}\text{O}_{\text{water}} = +7.5\text{‰}$.

916

917

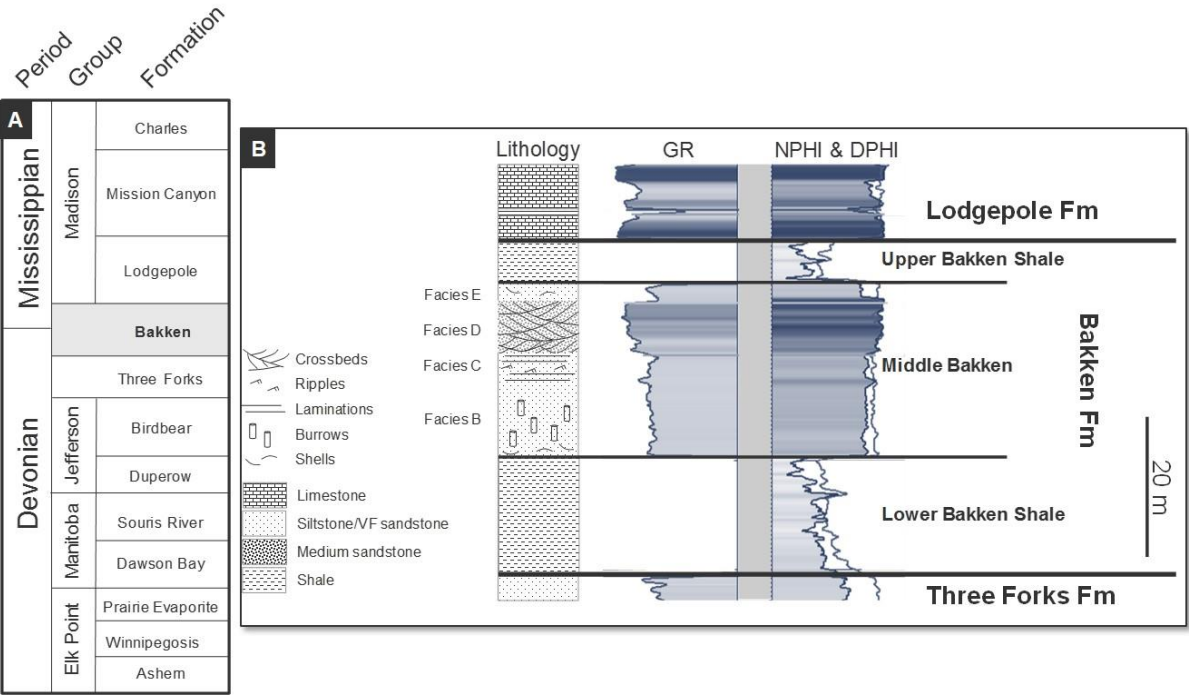
918 **Figure 1.**



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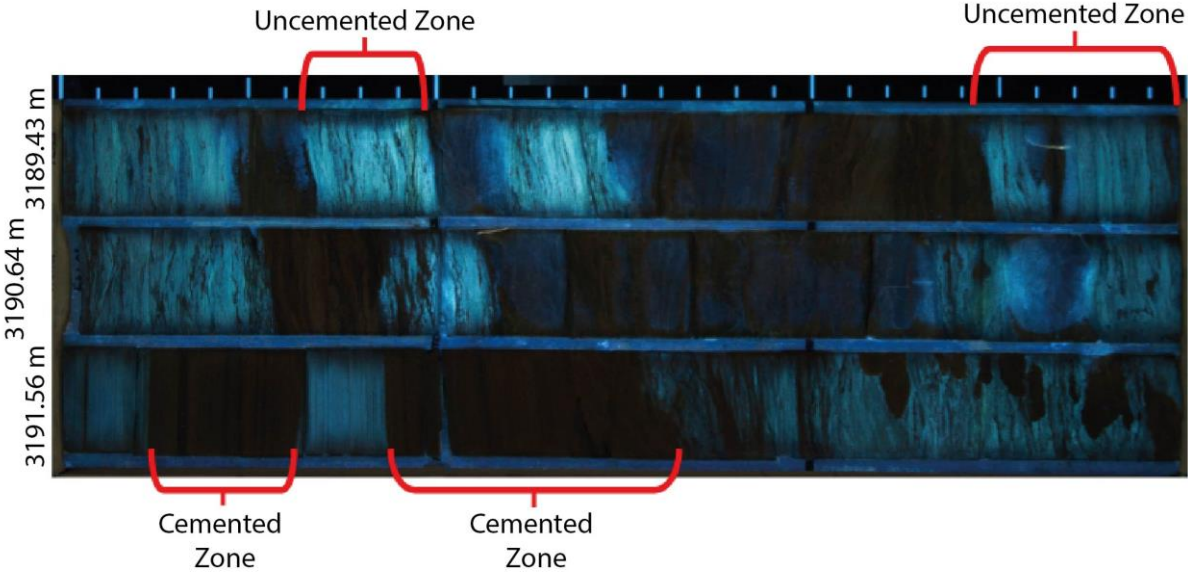
921 **Figure 2.**



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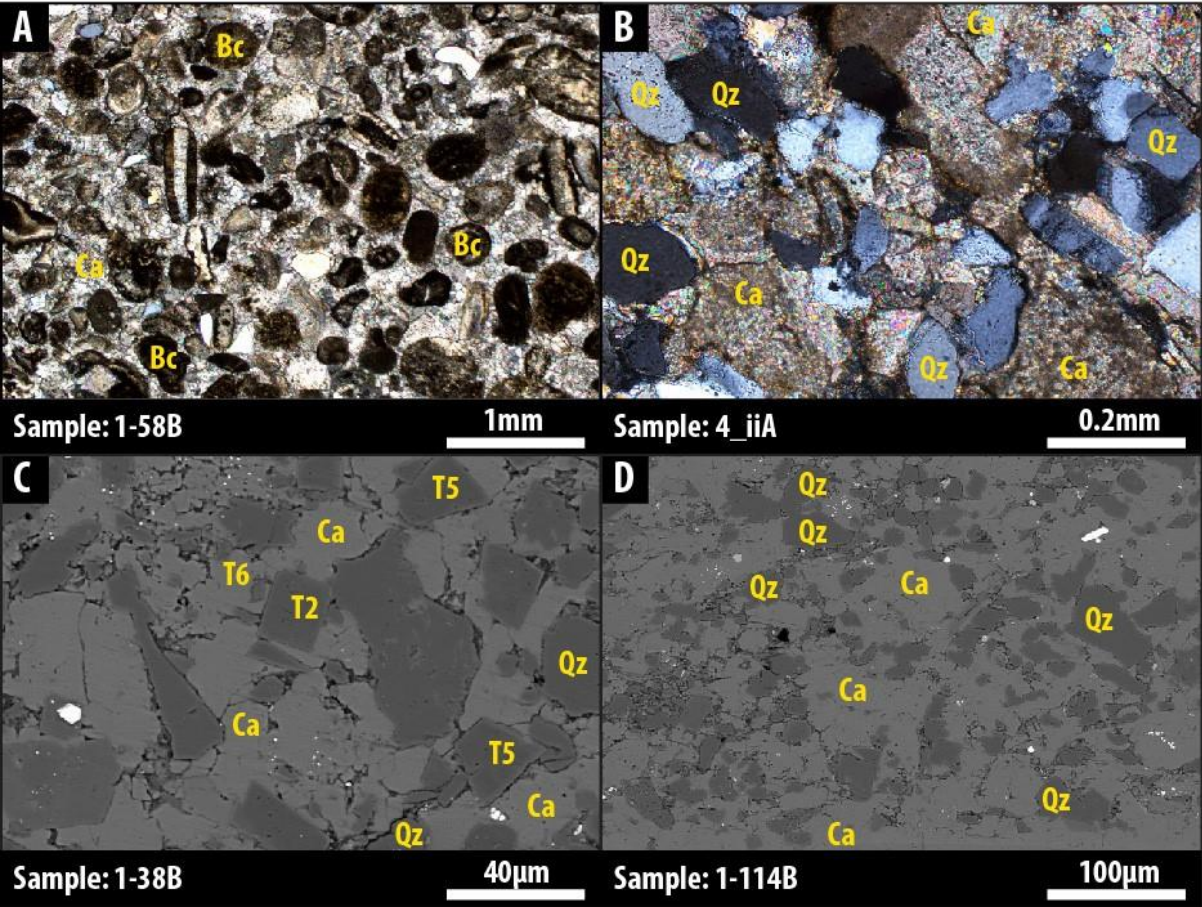
924 **Figure 3.**



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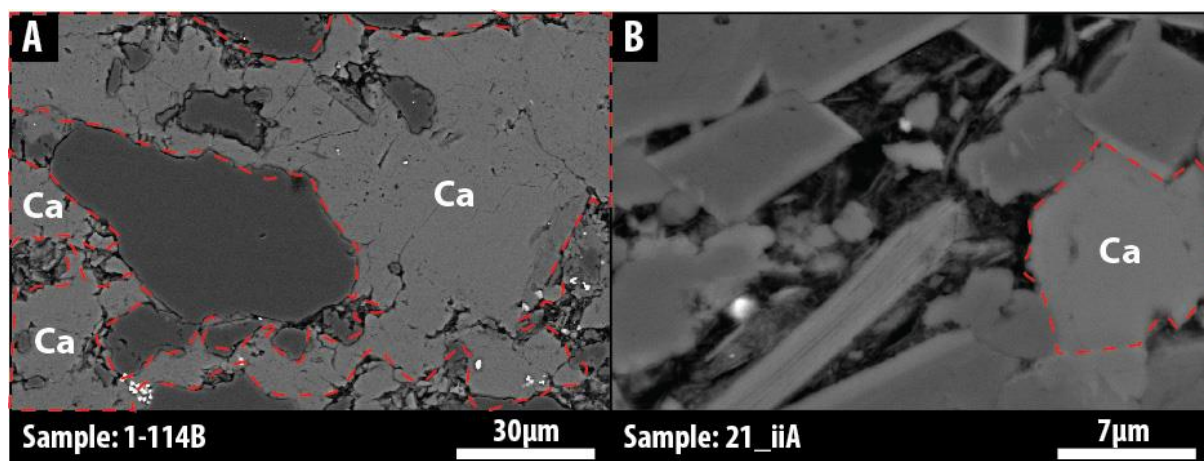
927 **Figure 4.**



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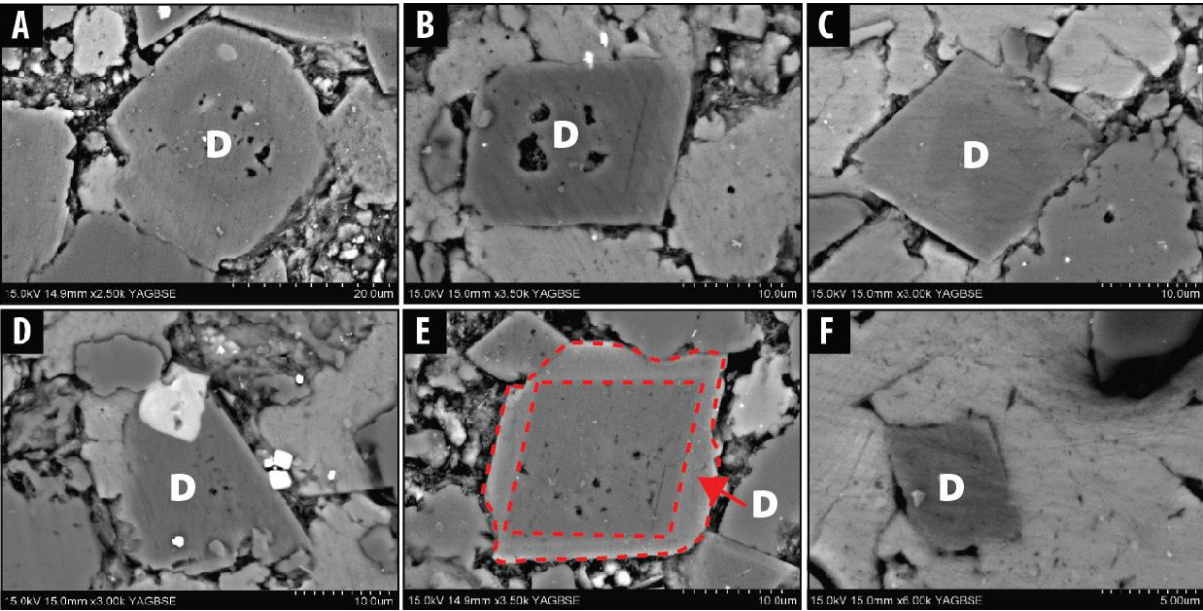
930 **Figure 5.**



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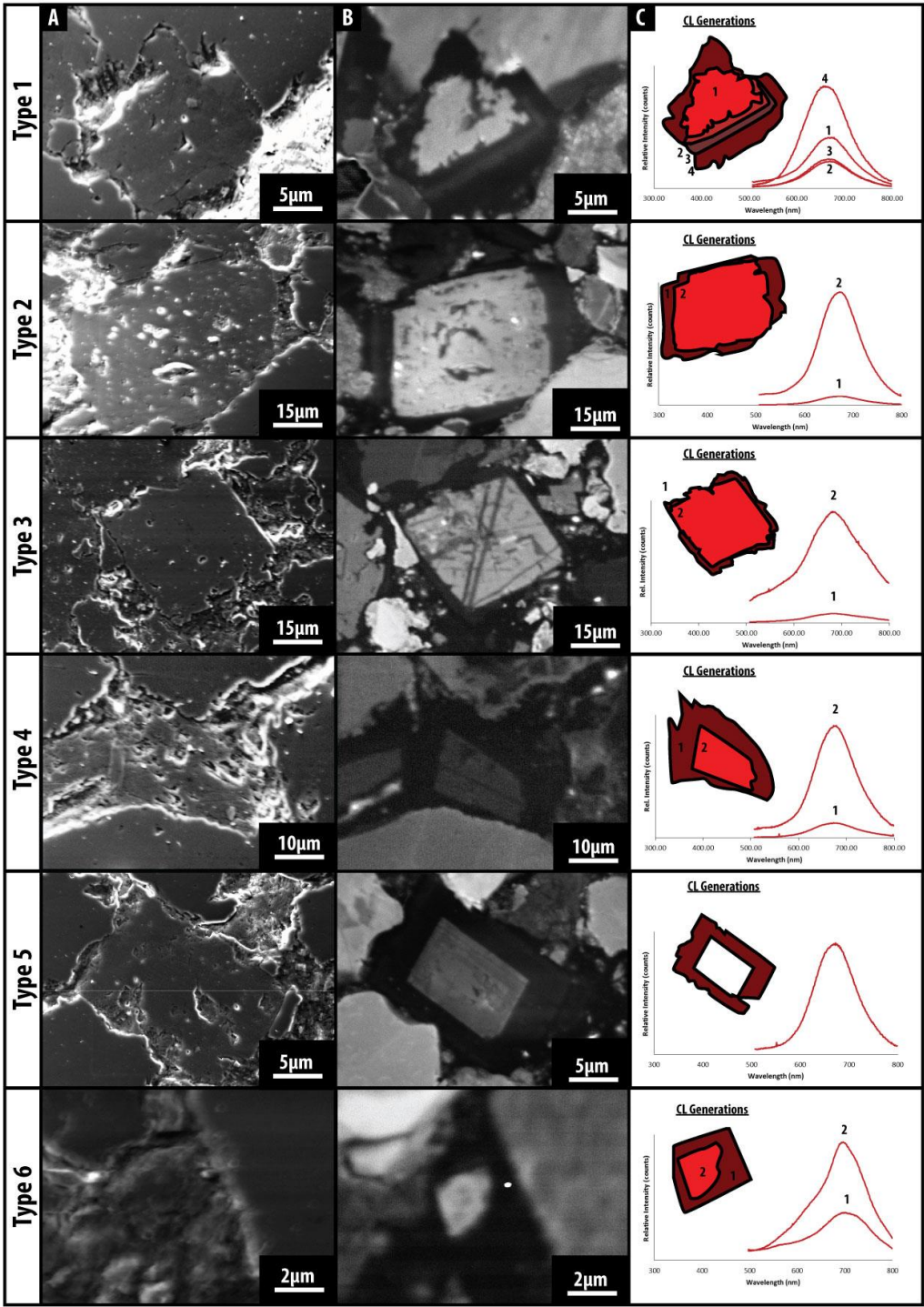
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933 **Figure 6.**

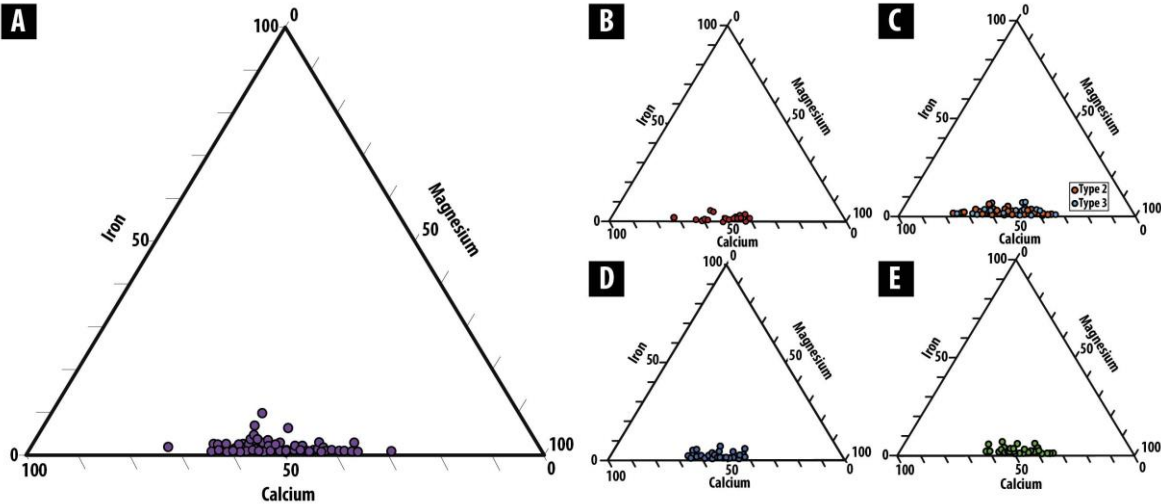


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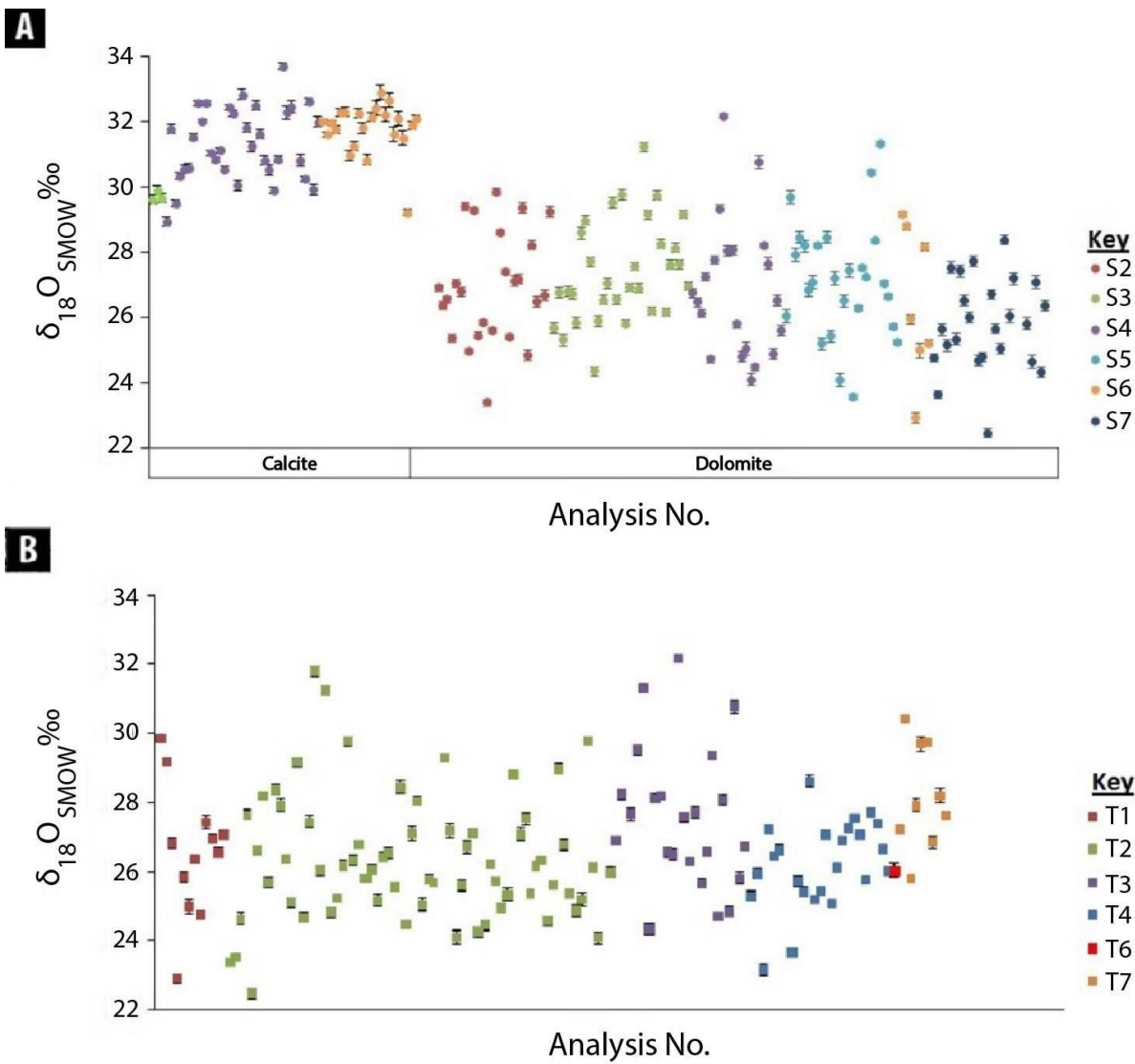
939 **Figure 8.**



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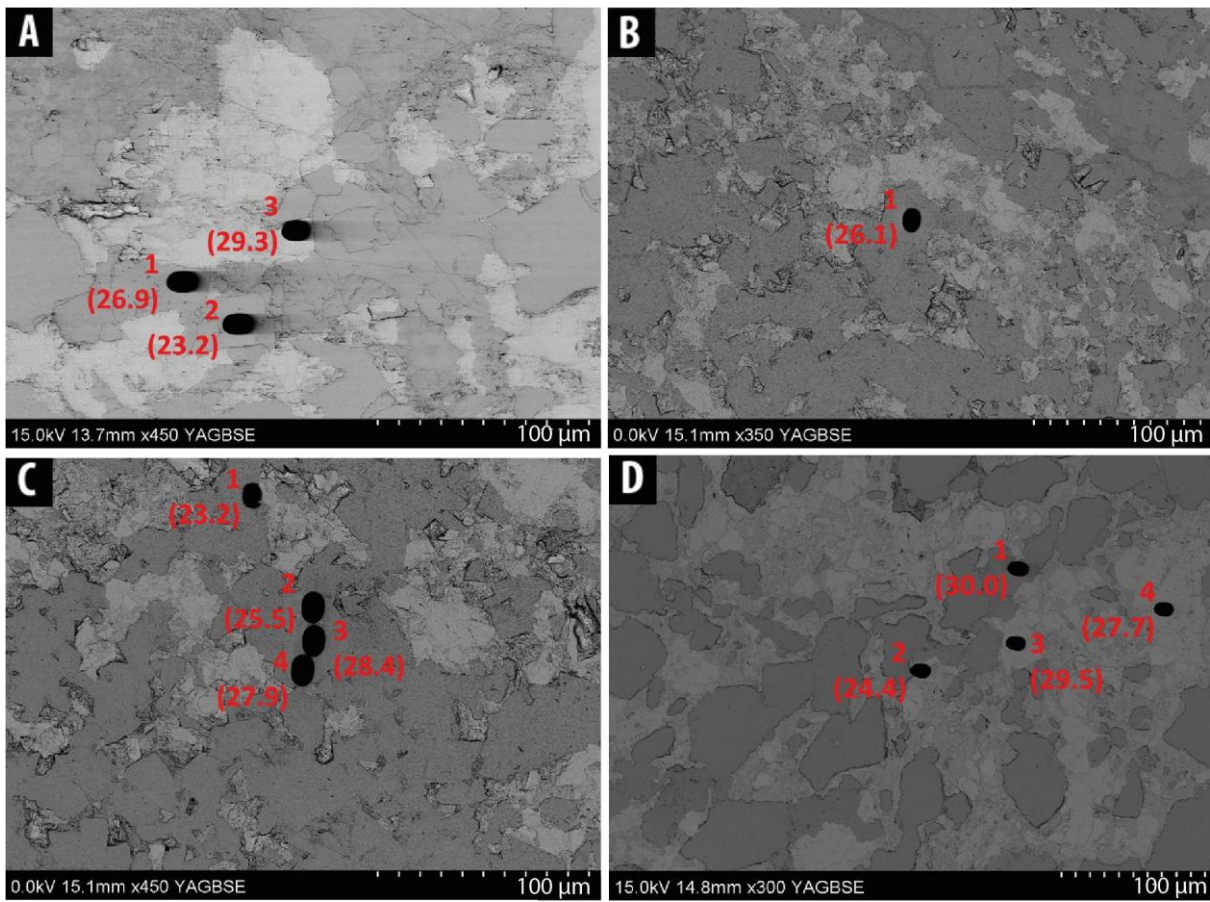
942 **Figure 9.**



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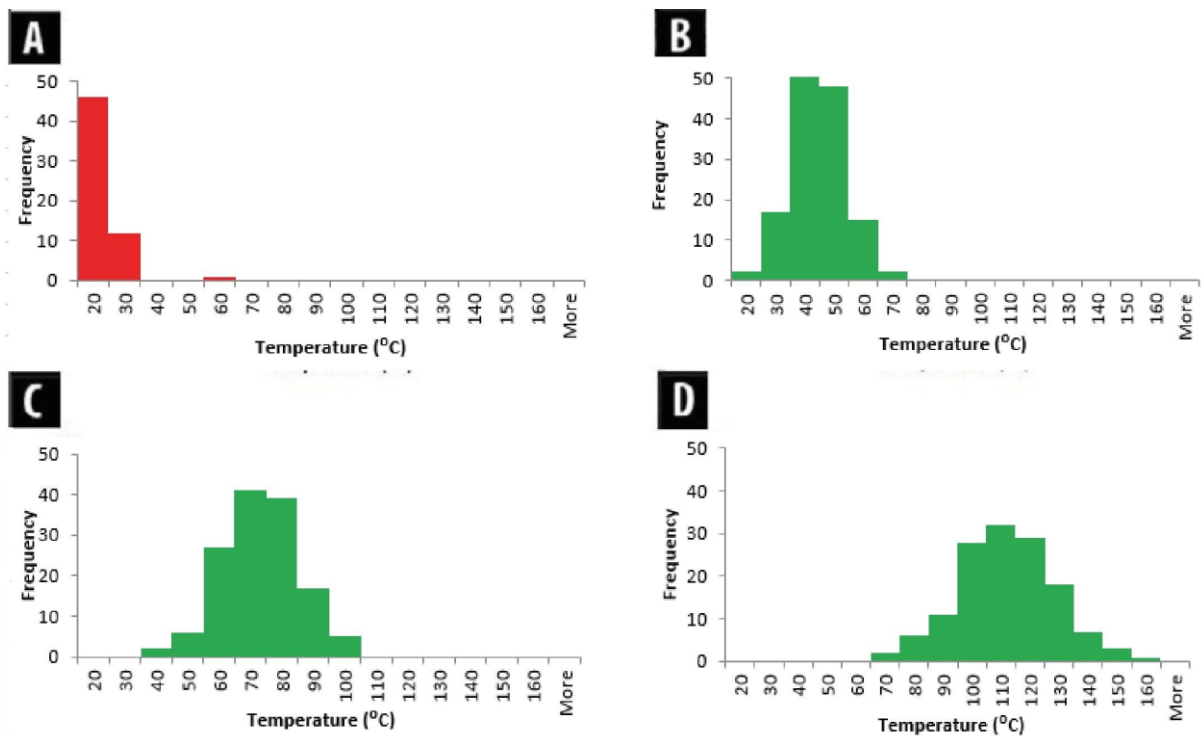
945 **Figure 10.**



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948 **Figure 11.**



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950

Table 1 – Mineralogical and bulk stable carbon and oxygen isotope data for calcite and dolomite obtained by sequential acid dissolution. Carbonate minerals calcite and dolomite were separated using conventional phosphoric acid digestion and gas-source mass spectrometric analyses on selected middle Bakken samples. Calcite is considered to be the CO₂ extracted after 3 hours of acid digestion at 25°C in a vacuum and dolomite is considered to be the CO₂ extracted after 24 hours at 100°C in a vacuum. Note that SIMS data from this study indicate that calcite and dolomite were not separated by this procedure. SIMS sample numbers are also shown.

Depth (m)	Sample No.	SIMS Sample No.	Facies	Oxygen and Carbon Isotopes by Sequential Acid Extraction				XRD Mineralogy (wt %)								
				Calcite @ 25°C		Dolomite @ 100°C		Quartz	Illite & Mica	Potassium Fspar	Plagioclase Fspar	Calcite	Dolomite	Pyrite	Halite	Chlorite
				Carbon ($\delta^{13}\text{C}_{\text{VPDB}}$)	Oxygen ($\delta^{18}\text{O}_{\text{VSMOW}}$)	Carbon ($\delta^{13}\text{C}_{\text{VPDB}}$)	Oxygen ($\delta^{18}\text{O}_{\text{VSMOW}}$)									
969.93	1-36B	7	E	-0.2	26.4	-0.5	25.7	42	13	4	5	3	29	2	2	0
970.02	1-37B	N/A	E	-0.8	26.1	-0.2	26.7	33	16	4	5	3	37	2	1	0
970.10	1-38B	N/A	E	-2.5	23.7	0.8	28.6	19	4	2	2	56	16	1	0	0
970.21	1-39B	N/A	E	-0.4	26.5	0.0	27.4	28	10	4	3	7	47	1	0	0
970.98	2_iiA	6	D2	3.1	25.8	1.5	28.7	46	3	4	2	31	14	1	0	0
971.00	4_iiA	5	D2	3.8	27.1	2.7	30.9	46	4	3	1	30	15	1	0	0
972.43	9_iiA	4	D1	3.3	26.0	3.6	30.8	38	5	6	3	36	12	0	0	0
	17_iiA	3	C	2.0	24.4	-0.3	26.1									
973.95								45	8	8	5	14	21	1	0	0
975.96	11_iiA	2	Grad	-0.5	25.3	-0.5	27.0	31	6	5	4	11	42	1	0	0
	1-113B	N/A	B	-3.2	25.4	-3.3	26.5	18	11	4	3	21	41	1	1	1
977.12																
977.17	1-114B	N/A	B	2.5	24.7	-2.1	19.8	29	12	4	3	37	12	2	0	1
977.27	1-115B	N/A	B	1.6	25.3	-0.3	26.1	23	10	3	3	53	5	3	0	1
977.36	1-116B	N/A	B	1.5	25.5	-0.3	27.1	30	13	4	3	36	9	3	0	1

- Supporting Online Material –

Geochemistry of calcite and dolomite in the Middle Bakken Formation, USA.

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Ion Microprobe Analysis of Carbonate Minerals

In situ oxygen isotope data were acquired in the WiscSIMS Laboratory at the University of Wisconsin–Madison by a CAMECA IMS 1280 large-radius multicollector ion microprobe (Kita et al., 2009, Valley and Kita 2009). Carbonate minerals calcite and dolomite were analyzed during four analytical sessions in October 2016 (**Error! Reference source not found.**). During the analytical sessions the $^{133}\text{Cs}^+$ primary ion beam had an intensity of ~1.2 nA generating a beam diameter of ~13 μm . The typical secondary $^{16}\text{O}^-$ ion intensity was $\sim 2.9 \times 10^9$ cps. Measurements were performed in multi-collector Faraday Cup mode and with conditions similar to those reported by Kozdon et al. (2009). The secondary O^- ions ($^{16}\text{O}^-$, $^{16}\text{O}^{1}\text{H}^-$, $^{18}\text{O}^-$) were detected by Faraday cup. Charging of the sample surface was compensated by Au-coating and an electron flood gun. Grains of the University of Wisconsin calcite standard, UWC-3 [$\delta^{18}\text{O}$ (VSMOW) of UWC-3 is 12.49‰ (± 0.03 ‰ 1 SD, n= 9)] was mounted at the centre of sample mounted in the polished block (Kozdon et al., 2009). Four consecutive measurements of UWC-3 calcite standard were performed before and after every set of 8–17 sample analyses. The 2 SD of a set of bracketing standard analyses is assigned as the reproducibility of the bracketed sample analyses. Detailed analytical protocols are described in Kita et al. (2009).

Table X – Full details of SIMS & SEM-WDS analyses for individual crystals. Data not included in the plots and interpretation are also included to show the full bracketed analyses. External precision (reproducibility) is reported for each bracket. The ‘Mineral/ Type/Comment’ column gives details of the analysis including dolomite phase type as a number e.g. type 1 is ‘1’, NF=Crystal was not found post-SIMS analysis, NC= Crystal was not composed of a carbonate mineral, Calcite = calcite crystal. What is “Er” type in that column? Can you annotate which Mass Biases were corrected using the calibration curve? Would it be possible/prudent to include the standard calibration measurements (up to you)?

No.	Sample ID	¹⁶ O (Gcps)	^{δ18} O ‰ measu red	2SE (int.)	Mass Bias	^{δ18} O ‰ VSMO W	2SD (ext.)	OH/O	Mineral / Type / Comment	CaO	MgO	FeO
Sample Mount No. 2. 13 μm beam, 1.2 nA intensity. October 6th 2015												
1	2 UWC3 G1	2.99	5.22	0.45								
2	2 UWC3 G1	3	5.04	0.45								
3	2 UWC3 G1	3.01	5.19	0.53								
4	2 UWC3 G2	2.97	5.2	0.5								
5	2-004	3.14	14.29	0.47	-12.28	26.9	0.21	0.003	2	51.93	51.44	0
6	2-005	3.07	15.38	0.45			0.21	0.005	NF			
7	2-006	3.01	13.75	0.46	-12.28	26.36	0.21	0.001	1	54.93	53.06	0.7
8	2-007	2.01	7.94	0.27	-5.41	13.41	0.21	0.001	NC			
9	2-008	2.91	13.95	0.53	-12.28	26.56	0.21	0.002	3			
10	2 UWC3 G1		5.34	0.54								
11	2 UWC3 G1		5.34	0.47								
12	2 UWC3 G1		5.15	0.54								
13	2 UWC3 G1		5.13	0.56								
		Average:	5.2	2SD:	0.21							
14	2-009	2.15	7.02	0.22	-5.41	12.5	0.25	0.002		39.95	61.79	0.0
15	2-009-2	2.04	8.14	0.3	-5.41	13.63	0.25	0.004	NC			
16	2-009-3	2.12	10.04	0.23	-5.41	15.54	0.25	0.005	NC			
17	2-011	3.09	13.41	0.39	-11.64	25.35	0.25	0.005	2	36.69	63.31	0.5
18	2-012	3.07	14.41	0.71	-12.3	27.05	0.25	0.006	1	39.16	62.72	0.0
19	2-013	3.05	14.15	0.45	-12.3	26.78	0.25	0.008	2			
20	2-017	2.89	17.4	0.45	-11.64	29.39	0.25	0.004	3	39.98	61.04	0.6
21	2-018	2.07	7.9	0.29	-5.41	13.38	0.25	0.006	NC			
22	2-061	2.08	10.35	0.52	-5.41	15.85	0.25	0.006	NC			
23	2-021	2.09	7.01	0.32	-5.41	12.49	0.25	0.005	NC			

24	2 UWC3 G1	2.85	5.13	0.47								
25	2 UWC3 G1	2.81	5.29	0.5								
26	2 UWC3 G1	2.9	5.01	0.48								
27	2 UWC3 G1	2.96	5.08	0.47								
		Average:	5.18	2SD:	0.25							
28	2-022	3.19	13.42	0.49			0.18	0.006	NF			
29	2-022a	3.17	12.32	0.43	-12.33	24.96	0.18	0.002	2	41.56	59.51	0.1
30	2-022b	3.03	16.59	0.49	-12.33	29.28	0.18	0.002	2			
31	2-024	3.06	12.81	0.43	-12.33	25.46	0.18	0.003	4	38.9	61.14	0.1
32	2-025	3.05	13.18	0.5	-12.33	25.83	0.18	0.004	3	37.46	62.69	0.1
33	2-026	3.11	12.2	0.45	-10.93	23.38	0.18	0.001	2	43.13	56.1	1.1
34	2-027	2.08	15.05	0.28	-5.45	20.61	0.18	0.010	NF			
35	2-028	3.2	15.79	0.53	-9.57	25.6	0.18	0.002	2	39.87	69.81	2.9
36	2-028a	2.09	6.97	0.22	-5.45	12.48	0.18	0.001	NC			
37	2-029	3.01	18.6	0.49	-10.93	29.86	0.18	0.004	1	38.61	60.56	1.0
38	2 UWC3 G1	2.84	5.12	0.5								
39	2 UWC3 G1	2.82	5.13	0.57								
40	2 UWC3 G1	2.9	5.26	0.45								
41	2 UWC3 G1	2.93	5.17	0.45								
		Average:	5.15	2SD:	0.18							
42	2-030	2.99	14.99	0.38			0.14	0.014	NF			
43	2-031	3.19	18.44	0.53			0.14	0.014	NF			
44	2-032	2.98	14.85	0.5			0.14	0.014	NF			
45	2-033	3.12	15.97	0.39	-12.28	28.6	0.14	0.006	4	41.41	59.02	0.1
46	2-034	2.86	17.24	0.58			0.14	0.003	NF			

47	2-035	3.07	13.65	0.53			0.14	0.007	NF			
48	2-036	2.94	15.39	0.49			0.14	0.004	NF			
49	2-036a	2.95	14.78	0.42	-12.28	27.39	0.14	0.004	4	42.72	57.84	1.7
50	2-038	3	12.82	0.57			0.14	0.005	NF			
51	2-039	3.02	12.82	0.52	-12.28	25.41	0.14	0.002	4	36.21	64.25	0.0
52	2 UWC3 G1	2.82	5.31	0.51								
53	2 UWC3 G1	2.8	5.27	0.58								
54	2 UWC3 G1	2.89	5.22	0.53								
55	2 UWC3 G1	2.94	5.16	0.49								
		Average:	5.2	2SD:								
56	2-040	3.12	14.48	0.52	-12.32	27.13	0.31	0.006	3	39.35	60.59	0.2
57	2-041	3.16	14.53	0.49			0.31	0.005	NF			
58	2-042	3.11	14.52	0.52	-12.32	27.18	0.31	0.002	3	36.17	63.79	0.3
59	2-043	3.04	15.06	0.49			0.31	0.004	NF			
60	2-043a	3.03	16.69	0.39	-12.32	29.37	0.31	0.004	2	36.92	63	0.1
61	2-044	3.12	12.89	0.58	-11.66	24.84	0.31	0.002	3	40.59	59.44	0.6
62	2-045	3.06	13.27	0.45			0.31	0.003	NF			
63	2-046	2.95	15.55	0.43	-12.32	28.22	0.31	0.005	3	36.21	63.65	0.0
64	2-047	3.03	13.84	0.42	-12.32	26.49	0.31	0.002	3	36.81	63.64	0.0
65	2-048	2.98	15.19	0.43	-2.21	17.44	0.31	0.006	2	38.17	60.2	0.0
66	2-049	3.03	14.03	0.58	-12.32	26.68	0.31	0.002	3	39.55	61.79	0.1
67	2-081	2.72	16.58	0.49	-12.32	29.26	0.31	0.002	2	39.07	61.38	0.0
68	2 UWC3 G1	2.83	4.82	0.5								
69	2 UWC3 G1	2.82	5.27	0.49								
70	2 UWC3 G1; Cs 127-128	2.92	5.13	0.52								
71	2 UWC3 G1	2.96	5.13	0.53								

		Average:	5.16	2SD:	0.31							
Sample Mount No. 3. 13 µm beam, 1.2 nA intensity. October 6th 2015												
72	3 UWC3 G1	2.94	5.02	0.5								
73	3 UWC3 G1	2.94	5.1	0.5 2								
74	3 UWC3 G2	2.92	5.02	0.5								
75	3 UWC3 G2	2.89	5.31	0.4 9								
76	3-012	2.05	4.78	0.3 4	-5.4	10.23	0.33	0.001	NC			
77	3-015	2.94	14.77	0.7 7	-11.63	26.72	0.33	0.004	2	52.64	47.32	0.2
78	3-016	3.03	13.9	0.5	-11.63	25.83	0.33	0.001	1	51.65	48.27	0.4
79	3-017	3	16.62	0.4 9	-11.63	28.59	0.33	0.003	3	50.81	48.94	0.0
80	3 UWC3 G1	2.84	5.3	0.5 2								
81	3 UWC3 G1	2.83	5.49	0.5 6								
82	3 UWC3 G1	2.94	5.13	0.5 2								
83	3 UWC3 G1	2.95	5.18	0.4 9								
		Average:	5.19	2SD:	0.33							
84	3-018	3.19	16.43	0.4 1	-12.19	28.97	0.29	0.001	2	50.64	49.55	0.1
85	3-021	2.98	15.19	0.4 4	-12.19	27.71	0.29	0.003	4	53.39	46.96	0.1

86	3-022	2.98	12.54	0.4 3	-11.53	24.35	0.29	0.003	3	50.75	48.8	0.4
87	3-023	2.94	13.38	0.5 3	-12.19	25.88	0.29	0.005	2	50.85	49.03	0.0
88	3-024	2.87	14.03	0.3 9	-12.19	26.54	0.29	0.004	1	52.43	48.64	0.0
89	3-025	3.07	17.98	0.4 5	-8.83	27.04	0.29	0.002	4	53.58	44.76	0.0
90	3-026	2.65	16.98	0.5 4	-12.19	29.53	0.29	0.002	3	98.6	1.33	0.2
91	3-026a	2.83	14.72	0.4 5	-11.53	26.55	0.29	0.003	3	51.79	49.36	0.6
92	3-027	2.72	17.22	0.4 2	-12.19	29.77	0.29	0.005	2	54.28	44.19	1.5
93	3 UWC3 G1	2.68	5.34	0.5 4								
94	3 UWC3 G1	2.68	5.51	0.5								
95	3 UWC3 G1	2.77	5.26	0.4 8								
96	3 UWC3 G1	2.91	5.18	0.5								
		Average:	5.3	2S D:	0.29							
97	3-028	3.06	13.29	0.5 4	-12.21	25.82	0.23	0.004	2	52.72	47.71	0.0
98	3-029	2.13	10.36	0.3	-5.32	15.77	0.23	0.008	NC			
99	3-030	2.02	11.45	0.2 8	-5.32	16.86	0.23	0.009	NC			
100	3-031	2.13	7.74	0.2	-5.32	13.14	0.23	0.001	NC			
101	3-032	3.23	14.37	0.5 3	-12.21	26.91	0.23	0.004	4	50.16	49.34	0.5
102	3-033	2.79	17.41	0.5 1			0.23	0.004	NF			
103	3-034	2.91	12.47	0.5 1			0.23	0.004	NF			

104	3-035	1.94	15.02	0.3	-5.32	20.45	0.23	0.001	NC			
105	3-036	2.94	12.58	0.4 3			0.23	0.004	NF			
106	3-037	3.08	15.2	0.5 2			0.23	0.005	NF			
107	3 UWC3 G1	2.88	5.19	0.5 3								
108	3 UWC3 G1	2.87	5.3	0.5								
109	3 UWC3 G1	2.87	5.16	0.4 3								
110	3 UWC3 G1	2.87	5.22	0.5 7								
		Average:	5.27	2S D:	0.23							
111	3-038	2.72	16.68	0.5			0.27	0.005	NF			
112	3-039	2.93	17.25	0.4 3			0.27	0.006	NF			
113	3-040	2.93	15.55	0.4 5			0.27	0.005	NF			
114	3-041	2.79	14.54	0.4 6			0.27	0.006	NF			
115	3-092	2.09	12.91	0.2 5	-5.31	18.32	0.27	0.001	NC			
116	3-093	3	15.58	0.4 8	-12.2	28.13	0.27	0.004	3	52.56	46.99	0.9
117	3-096	2.6	17.09	0.5 1	-12.2	29.66	0.27	0	2	98.55	1.16	0.2
118	3-097	2.87	15.09	0.5 5	-12.2	27.63	0.27	0.003	2	53.57	46.54	3.5
119	3 UWC3 G1	2.72	5.42	0.5 3								
120	3 UWC3 G1	2.69	5.55	0.5								

121	3 UWC3 G1; Cs 131-132	2.78	5.23	0.5 1								
122	3 UWC3 G1; Cs 132-133	2.94	5.18	0.4 1								
		Average:	5.28	2S D:	0.27							
126	3-098	3.29	16.62	0.4 7	-12.19	29.16	0.26	0.002	1	53.61	41.58	4.5
127	3-099	3.23	14.44	0.5 4	-12.19	26.95	0.26	0.020	1	50.64	47.75	1.7
128	3-091	2.82	17.36	0.5 4	-12.19	29.91	0.26	0.005	Calcite	97.25	2.54	0.1
129	3-090	3.19	15.1	0.4 4	-12.19	27.62	0.26	0.002	6	51.26	48.1	1.1
130	3-089	3.04	13.65	0.4 5	-12.19	26.15	0.26	0.005	2	65.33	36.39	0.2
131	3-088	3.06	15.73	0.5 7	-12.19	28.26	0.26	0.005	2	54.21	43.54	3.0
132	3-087	2.72	17.08	0.6 1	-12.19	29.63	0.26	0.003	Calcite	98.77	1.32	0.4
133	3-086	3.19	17.19	0.5 4	-12.19	29.74	0.26	0.002	6			
134	3-085	1.94	11.54	0.2 6	-5.3	16.93	0.26	0.001	NC			
135	3-084	2.02	9.39	0.2	-5.3	14.77	0.26	0.001	NC			
136	3-084a	2.09	3.61	0.2 9	-5.3	8.95	0.26	0.000	NC			
137	3-084b	3.03	13.8	0.4 6	-12.09	26.2	0.26	0.002	2	52.39	47.48	0.5
138	3-083	2.92	16.61	0.4 5	-12.19	29.15	0.26	0.003	2	51.34	49.07	0.6
139	3-081	2.97	15.22	0.5 1			0.26	0.004	3	49.49	50.29	0.0
140	3-080	2.98	15.04	0.5 7	-12.19	27.57	0.26	0.005	3	51.46	49.14	0.0
141	3-080a	2.85	14.38	0.5	-12.19	26.89	0.26	0.004	3	54.12	45.84	0.1

142	3-080b	3.03	18.67	0.3 9	-12.19	31.23	0.26	0.004	2	53.89	44.37	2.8
143	3 UWC3 G1	2.76	5.18	0.4 7								
144	3 UWC3 G1	2.73	5.3	0.5 1								
145	3 UWC3 G1	2.72	5.27	0.3 8								
146	3 UWC3 G1	2.71	5.25	0.5 6								
		Average:	5.3	2S D:	0.26							
Sample Mount No. 4. 13 µm beam, 1.2 nA intensity. October 7th 2015												
147	4 UWC3 G1	2.84	5.03	0.5								
148	4 UWC3 G2	2.87	5.37	0.5 5								
149	4 UWC3 G2	2.86	5.34	0.5 2								
150	4 UWC3 G2	2.87	5.19	0.5 1								
151	4-004	2.87	16.2 9	0.5 4	-12.3	28.94	0.26	0.002	Calcite	99.41	0.59	0.0
152	4-005	2.97	14.1 1	0.5 6	-12.3	26.74	0.26	0.006	3	29.56	70.59	0.1
153	4-006	2.72	19.1	0.5 6	-12.3	31.79	0.26	0.003	2	96.84	3.53	0.0
154	4-007	3.12	14.5 2	0.3 3	-11.64	26.47	0.26	0.001	4	43.54	56.22	0.3
155	4-008	2.11	5.18	0.2 1	-5.41	10.65	0.26	0.000	NC			

156	4-009	2.94	13.4 9	0.5 8	-12.3	26.11	0.26	0.002	4	42.06	57.74	0.0
157	4-010	3.03	14.6 1	0.6 3	-12.3	27.25	0.26	0.003	4	40.07	59.27	0.6
158	4-011	2.54	19.2 6	0.4 2				0.004	Er	95.32	3.47	
159	4 UWC3 G2	2.83	5.1	0.5 6								
160	4 UWC3 G2	2.85	5.12	0.4 8								
161	4 UWC3 G2	2.86	5.27	0.5 2								
162	4 UWC3 G2	2.89	5.04	0.5 3								
		Average:	5.19	2S D:	0.19							
163	4-012	3.11	12.6 7	0.4 4	-11.75	24.71	0.22	0.008	3	40.07	59.27	0.6
164	4-013	2.9	16.7 2	0.4 5	-12.41	29.5	0.22	0.002	Calcite	96.74	0.9	1.1
165	4-014	2.81	17.5 6	0.5 3	-12.41	30.35	0.22	0.003	Calcite	97.44	1.78	0.3
166	4-015	3.12	15	0.4 4	-12.41	27.76	0.22	0.003	2	42.26	57.67	0.2
167	4-016	3.32	16.5 7	0.5 7	-12.41	29.34	0.22	0.003	3	42.62	57.56	0.3
168	4-017	2.84	17.7 7	0.7 1	-12.41	30.56	0.22	0.010	Calcite	96.72	3.11	0.6
169	4-018	2.94	17.8 1	0.5 4	-12.41	30.6	0.22	0.003	Calcite	94.79	2.96	1.0
170	4-018a	3	18.7 4	0.5 9	-12.41	31.54	0.22	0.003	Calcite	95.49	4.4	0.0
171	4 UWC3 G2	3.19	4.98	0.5 9								

172	4 UWC3 G2	3.2	5.14	0.4 5								
173	4 UWC3 G2	3.15	4.97	0.4 9								
174	4 UWC3 G2	3.12	4.95	0.4 8								
		Average:	5.07	2S D:	0.22							
175	4-019	3.04	19.7 1	0.5 2	-12.46	32.58	0.15	0.002	Calcite	96.63	3.63	0.1
176	4-020	2.98	19.1 6	0.5 3	-12.46	32.03	0.15	0.002	Calcite	98.56	3.27	0.0
177	4-021	2.95	19.7 1	0.5 1	-12.46	32.58	0.15	0.002	Calcite	98.64	3.09	0.0
178	4-022	2.8	18.2	0.5 7	-12.46	31.05	0.15	0.003	Calcite	97.4	3.76	0.4
179	4-023	3.09	18	0.4 6	-12.46	30.85	0.15	0.002	Calcite	97.83	2.69	0.0
180	4-024	3.05	20	0.4 8	-11.81	32.18	0.15	0.001	3	53.01	46.48	0.6
181	4-025	3.08	18.2 9	0.5 8	-12.46	31.14	0.15	0.004	Calcite	95.31	4.3	0.0
182	4-026	3.14	17.7 1	0.4 6	-12.46	30.56	0.15	0.002	Calcite	95.67	4.53	0.0
183	4 UWC3 G2	3.26	5.05	0.5 1								
184	4 UWC3 G2	3.28	4.91	0.4 7								
185	4 UWC3 G2	3.16	5.04	0.5 1								
186	4 UWC3 G2	3.14	5.08	0.4 4								
		Average:	5.01	2S D:	0.15							

187	4-027	2.96	19.6 1	0.5 1	-12.45	32.46	0.18	0.000	Calcite	96.81	3.25	0.0
188	4-066	2.92	18.5 2	0.4 8	-5.8	24.46	0.18	0.002	2			
189	4-074	2.95	17.4 3	0.4 5	-12.45	30.25	0.18	0.004	Calcite	92.15	7.51	0.0
190	4-074a	3.44	15.4 1	0.3 5	-12.45	28.21	0.18	0.001	3	29.05	72.06	0.0
191	4-074b	3.07	19.7 7	0.4 6	-12.45	32.62	0.18	0.003	Calcite	94.64	5.6	0.0
192	4-028	3.13	19.4 1	0.4 9	-12.45	32.26	0.18	0.001	Calcite	98.12	1.63	0.1
197	4 UWC3 G2	3.24	4.93	0.5 4								
198	4 UWC3 G2	3.25	5.01	0.5 4								
199	4 UWC3 G2	3.14	5.08	0.5 1								
200	4 UWC3 G2	3.01	5.19	0.5								
		Average:	5.03	2S D:	0.18							
201	4-029	2.89	17.3 5	0.5 6	-12.33	30.05	0.3	0.000	Calcite	97.09	2.66	0.2
202	4-030	2.81	20.1 1	0.4 4	-12.33	32.85	0.3	0.002	Calcite	95.89	4.69	0.0
203	4-031	3.03	15.3 7	0.4 2	-12.33	28.05	0.3	0.004	2	43.23	57.03	0.0
204	4-032	2.7	19.1	0.5 4	-12.33	31.83	0.3	0.004	Calcite	96.96	4.33	0.0
205	4-033	2.82	18.5 3	0.4 7	-12.33	31.25	0.3	0.003	Calcite	98.43	2.05	0.3
206	4-034	3.08	15.3 9	0.4 6	-12.33	28.07	0.3	0.003	3	43.63	56.02	0.0
207	4-035	2.91	19.7 8	0.4 9	-12.33	32.51	0.3	0.001	Calcite	98.43	2.62	0.0

208	4-035a	2.73	18.8 9	0.5 3	-12.33	31.61	0.3	0.004	Calcite	99.73	2.26	0.0
209	4-036	2.86	18.1 1	0.5 1	-12.33	30.82	0.3	0.001	Calcite	99.77	0	0.0
210	4 UWC3 G2	3.02	5.33	0.5 5								
211	4 UWC3 G2	3.05	5.18	0.4 5								
212	4 UWC3 G2	3.04	5.35	0.5 2								
213	4 UWC3 G2	3.06	5.11	0.4 7								
		Average:	5.15	2S D:	0.3							
Sample Mount No. 4. 13 µm beam, 1.2 nA intensity. October 7th 2015*												
214	4 UWC3 G2	3.09	5.3	0.4 6								
215	4 UWC3 G2	2.99	5.17	0.5 5								
216	4 UWC3 G2	2.95	5.16	0.5 3								
217	4 UWC3 G2	2.97	5.24	0.5 1								
218	4-038	2.16	4.78	0.2 3	-5.34	10.18	0.21	0.001	NC			
219	4-039	2.89	19.25	0.5 3	-6.37	25.78	0.21	0.001	6	95.97	3.56	0.0
220	4-048	2.89	17.3	0.4 6	-12.23	29.9	0.21	0.002	Calcite	99.15	0.89	0.5
221	4-051	2.74	18.27	0.4 8	-12.23	30.88	0.21	0.005	Calcite	98.53	1.41	0.5
222	4-056	2.38	21.05	0.5 4	-12.23	33.7	0.21	0.000	Calcite	95.62	3.99	0.2

223	4 UWC3 G2	2.69	5.49	0.5 1								
224	4 UWC3 G2	2.91	5.25	0.5 2								
225	4 UWC3 G2	3	5.19	0.4 7								
226	4 UWC3 G2	3.06	5.22	0.4 5								
		Average:	5.25	2SD:	0.21							
227	4-057	2.98	19.57	0.5 3	-12.32	32.29	0.38	0.000	Calcite	96.53	3.34	0.0
228	4-058	3.23	12.41	0.4 1	-12.32	25.04	0.38	0.008	2	41.6	59.03	0.0
229	4-059	2.98	19.76	0.5 8	-12.32	32.48	0.38	0.000	Calcite	96.4	2.72	0.4
230	4-061	3.22	12.15	0.4 3	-11.66	24.1	0.38	0.002	2	38.76	60.38	0.6
231	4-069	2.27	12.13	0.2 3	-5.43	17.66	0.38	0.000	NC			
232	4-069a	3.23	12.25	0.4 6	-12.32	24.88	0.38	0.001	2	38.39	62.63	0.4
233	4-070	3.02	19.52	0.5 2	-10.92	30.77	0.38	0.001	3	97.11	3.82	0.1
234	4-072	3.02	18.12	0.5 5	-12.32	30.82	0.38	0.000	Calcite	95.66	2.9	1.3
235	4-078	3.28	14.99	0.5	-12.32	27.65	0.38	0.003	3	40.19	60.06	0.0
236	4-086	2.29	13.86	0.2 8	-5.43	19.4	0.38	0.003	NC			
237	4 UWC3 G2	3.09	5	0.4								
238	4 UWC3 G2	3.07	5.21	0.5								
239	4 UWC3 G2	3.11	5.08	0.5								

240	4 UWC3 G2	3.14	4.86	0.4 8								
		Average:	5.16	2SD:	0.38							
251	4-092	3.11	18.29	0.4 7	-12.33	31	0.32	0.002	Calcite	97.07	3.63	0.0
252	4-097	3.17	17.24	0.5 3	-12.33	29.94	0.32	0.002	Calcite	98.76	1.45	0.2
253	4-097a	3.11	19.27	0.5 2	-12.33	31.99	0.32	0.002	Calcite	97.3	3.08	0.2
254	4-089	3.53	13.63	0.4 9	-11.67	25.6	0.32	0.016	2	40.25	58.72	0.4
255	4-042; Cs 141-139	3.27	12.17	0.5 9	-12.33	24.81	0.32	0.003	2	41.28	58.44	0.3
256	4-043	2.93	17.82	0.5 9	-12.33	30.53	0.32	0.003		94.62	4.76	0.0
257	4-100	2.19	14.22	0.3 4	-5.44	19.77	0.32	0.009	NC			
258	4-082	3.31	12.92	0.5 8	-11.67	24.88	0.32	0.001	2	39.81	60.54	0.3
259	4-082a	3.26	13.87	0.5 7	-12.33	26.52	0.32	0.002	2	39.03	60.9	0.0
260	4 UWC3 G2	3.09	5.35	0.4 8								
261	4 UWC3 G2	3.09	5.28	0.5 1								
262	4 UWC3 G2	3.1	5.21	0.5 5								
263	4 UWC3 G2	3.12	5.23	0.5 7								
		Average:	5.15	2SD:	0.32							
Sample Mount No. 5. 13 µm beam, 1.2 nA intensity. October 8th 2015												

264	5 UWC3 G1	2.86	4.86	0.4 9								
265	5 UWC3 G2	2.89	4.96	0.5								
266	5 UWC3 G2	2.98	4.62	0.5 4								
267	5 UWC3 G2	2.99	4.82	0.4 6								
268	5-015	3.04	16.74	0.2 1	-12.57	29.69	0.39	0.004	6	52.16	46.54	1.2
269	5-015a	3.2	15	0.4 5	-12.57	27.92	0.39	0.004	6	50.99	48.25	1.0
270	5-015b	3.12	15.54	0.3 7	-12.57	28.46	0.39	0.004	6	50.41	48.45	1.0
271	5-015c	3.18	15.26	0.4 6	-12.57	28.19	0.39	0.005	6	51.26	47.73	1.1
272	5-089	2.12	9.08	0.3 2	-5.68	14.84	0.39	0.002	NC			
273	5-015d	3.16	13.94	0.6 2	-12.57	26.84	0.39	0.005	6	44.91	58.97	1.7
274	5-100	3.05	13.6	0.5 1	-12.57	26.51	0.39	0.009	3	52.34	47.53	0.0
275	5-100a	2.95	14.52	0.4 1	-12.57	27.43	0.39	0.007	1	50.27	48.1	1.3
276	5 UWC3 G1	2.8	5.27	0.4 8								
277	5 UWC3 G1	2.82	5.04	0.4 8								
278	5 UWC3 G1	2.98	4.92	0.4 8								
279	5 UWC3 G1	3.04	4.78	0.4 9								
		Average:	4.91	2SD:	0.39							

280	5-099	3.19	11.31	0.5 3	-12.47	24.08	0.39	0.002	2	51.59	48.66	0.0
281	5-098	3.12	14.4	0.5	-12.47	27.21	0.39	0.005	4	54.05	46.27	0.0
282	5-028	2.18	22.62	0.2 5	-5.58	28.36	0.39	0.002	NC			
283	5-028a	2.2	22.45	0.2 7	-5.58	28.19	0.39	0.002	NC			
284	5-028b	2.2	22.1	0.3 1	-5.58	27.84	0.39	0.002	NC			
285	5-023	3.12	14.29	0.3 5	-12.47	27.09	0.39	0.007	2	51.27	49.06	0.0
286	5-004	3.31	13.24	0.5 7	-12.47	26.03	0.39	0.009	5	50.91	47.78	1.8
287	5-005	2.18	8.78	0.3	-5.58	14.44	0.39	0.001	NC			
288	5-078	2.9	12.4	0.5 6	-12.47	25.18	0.39	0.004	2	51.05	48.85	0.2
289	5 UWC3 G1	2.59	4.94	0.5 1								
290	5 UWC3 G1	2.67	5.01	0.4 6								
291	5 UWC3 G1	2.89	4	0.4 72								
292	5 UWC3 G1	2.82	5.32	0.4 4								
293	5 UWC3 G1	2.87	4.81	0.5 4								
		Average:	5.01	2SD:	0.39							
294	5-080	2.93	15.67	0.4 7	-12.43	28.45	0.37	0.005	2	50.92	48.96	0.3
295	5-081	3	12.69	0.4 6	-12.43	25.43	0.37	0.002	4	51.83	47.53	0.5
296	5-082	2.1	11.3	0.2 5	-5.54	16.93	0.37	0.001	NC			

297	5-084	2.97	17.5	0.5 4			0.37	0.009	Er			
298	5-053	1.86	10.58	0.2 7	-5.54	16.21	0.37	0.002	NC			
299	5 UWC3 G1	2.67	5.01	0.4 6								
300	5 UWC3 G1	2.75	5.07	0.5 1								
301	5 UWC3 G1	2.82	5.34	0.5 4								
302	5 UWC3 G1	2.87	4.94	0.4 6								
		Average:	5.05	2SD:	0.37							
Sample Mount No. 1. 13 µm beam, 1.2 nA intensity. October 8th 2015												
303	1 UWC3 G1	2.87	5.12	0.4 9								
304	1 UWC3 G1	2.9	5.01	0.4 6								
305	1 UWC3 G1	2.93	5.24	0.5 3								
306	1 UWC3 G1	2.93	4.87	0.4 7								
307	1-079	3	14.05	0.3 3	-12.56	26.95	0.39	0.006	3	49.35	48.35	1.6
308	1-073	3.11	11.75	0.5 2	-11.16	23.17	0.39	0.002	4	47.48	51.42	0.0
309	1-072	3.07	14.41	0.5 1	-12.56	27.32	0.39	0.002	2	49.43	50.23	0.7
310	1-071	3.14	12.58	0.4 7	-12.56	25.46	0.39	0.005	3	49.92	50.55	0.0
311	1-071a	3.1	16.18	0.4 8	-11.9	28.42	0.39	0.005	2	46.15	53.38	0.3

312	1-071b	3.17	15.02	0.3 4	-12.56	27.93	0.39	0.004	2	48.36	51.38	0.7
313	1-074	3.24	13.91	0.5 1	-12.56	26.81	0.39	0.007	4	48.99	50.59	0.8
314	1-075	3.31	13.71	0.5 1	-11.9	25.93	0.39	0.004	4	45.64	54.67	0.0
315	1 UWC3 G1	3.17	4.91	0.5								
316	1 UWC3 G1	3.11	4.74	0.4 9								
317	1 UWC3 G1	2.98	4.74	0.4 6								
318	1 UWC3 G1	2.98	4.69	0.4 6								
		Average:	4.92	2SD:	0.39							
319	1-051	3.06	13.79	0.5 5	-11.96	26.06	0.28	0.004	2	47.21	52.91	0.5
320	1-051a	3.08	13.7	0.4 8	-10.5	24.46	0.28	0.006	2	46.63	53.15	1.9
321	1-051b	3.1	13.03	0.4 7	-12.61	25.98	0.28	0.007	2	47.02	53.07	0.0
322	1-052	3.13	13.37	0.5 5			0.28	0.008	Er			
323	1-053	3.15	11.64	0.4 7	-12.61	24.56	0.28	0.006	2	47.41	52.78	0.2
324	1-054	3.28	13.09	0.4 1	-12.61	26.03	0.28	0.002	2			
325	1-054a	3.23	13.23	0.5	-12.61	26.18	0.28	0.008	2	49.23	50.94	0.6
326	1-054b	3.2	12.84	0.4 4	-12.61	25.78	0.28	0.004	2	41.88	58.18	0.3
327	1-054c	3.16	12.66	0.4 6	-12.61	25.6	0.28	0.001	2	72.54	26.83	1.4
328	1-054d	3.11	13.95	0.4 6	-12.61	26.91	0.28	0.001	2	63.55	36	0.7

329	1 UWC3 G1	2.97	4.96	0.5 4								
330	1 UWC3 G1	3.03	4.8	0.5 6								
331	1 UWC3 G1	3.09	5	0.5 3								
332	1 UWC3 G1	3.14	5.07	0.5 2								
		Average:	4.86	2SD:	0.28							
333	1-067	3.33	13.28	0.5 9	-12.52	26.13	0.28	0.004	2	47.59	52.22	0.9
334	1-067a	2.87	16.88	12. 49	-12.52	29.78	0.28	0.006	2	49.33	50.53	0.2
335	1-067b	3.09	13.57	0.6 6	-12.52	26.42	0.28	0.001	2	47.32	52.88	0.4
336	1-067c	3.09	11.43	0.5 1	-12.52	24.25	0.28	0.008	2	48.78	52.04	0.0
337	1-067d	3.07	14.91	0.4 5	-11.86	27.1	0.28	0.004	2	47.31	53.36	0.7
338	1-067e	3.09	13.76	0.4 5	-12.52	26.61	0.28	0.007	2	48.51	52.41	1.9
339	1-067f	3.07	12.72	0.4 9	-12.52	25.56	0.28	0.007	2	49.24	50.82	0.3
340	1-067g	3.12	12.27	0.5	-12.52	25.11	0.28	0.002	2			
341	1 UWC3 G1	2.85	4.99	0.4 7								
342	1 UWC3 G1	2.83	5.18	0.5 4								
343	1 UWC3 G1	2.83	4.76	0.4 7								
344	1 UWC3 G1	2.8	4.9	0.5 6								

		Average:	4.96	2SD:	0.28								
Sample Mount No. 7. 13 µm beam, 1.2 nA intensity. October 8th 2015													
345	7 UWC3 G1	2.86	5.08	0.55									
346	7 UWC3 G1	2.88	5.12	0.51									
347	7 UWC3 G1	2.85	5.06	0.49									
348	7 UWC3 G1	2.8	5.09	0.53									
349	7 UWC3 G1	2.87	5.24	0.46									
350	7-004	3.25	12.67	0.45	-11.79	24.75	0.25	0.009	1	50.03	49.95	0.3	
351	7-005	3.21	11.58	0.46	-11.79	23.65	0.25	0.010	4	51.22	48.5	0.6	
352	7-006	2.25	7.01	0.3	-5.56	12.63	0.25	0.001	NC				
353	7-020	2.36	10.81	0.23	-5.56	16.46	0.25	0.001	NC				
354	7-021	2.11	7.22	0.3	-5.56	12.85	0.25	0.002	NC				
355	7-023	2.33	8.82	0.27	-5.56	14.45	0.25	0.001	NC				
356	7-024	2.33	12.7	0.32	-5.56	18.35	0.25	0.002	NC				
357	7-060	2.36	12.84	0.28	-5.56	18.5	0.25	0.001	NC				
358	7 UWC3 G1	3.23	4.79	0.51									
359	7 UWC3 G1	3.15	4.94	0.53									

360	7 UWC3 G1	3.03	4.97	0.3 9								
361	7 UWC3 G1	2.91	5.02	0.4								
		Average:	5.04	2SD:	0.25							
362	7-048	3.15	14.95	0.5 5	-12.43	27.72	0.33	0.007	3	52.67	45.85	0.0
363	7-047	3.1	13.24	0.4 8	-12.43	25.99	0.33	0.007	4	51.45	48.36	0.2
364	7-041	2.99	13.77	0.4 4	-12.43	26.53	0.33	0.007	3	51.87	48.16	0.1
365	7-041a	1.96	5.55	0.2 6	-5.54	11.15	0.33	0.002	NC			
366	7-040	2.09	13.5	0.3 7	-5.54	19.15	0.33	0.002	NC			
367	7-100	2.94	13.59	0.4 4	-12.43	26.34	0.33	0.008	2	51.3	49.63	0.0
368	7-099	3.03	11.6	0.5 7	-12.43	24.33	0.33	0.010	3	52.11	48.4	0.0
369	7-098	2.13	7.3	0.2 5	-5.54	12.91	0.33	0.003	NC			
370	7 UWC3 G1	2.86	5.18	0.4 5								
371	7 UWC3 G1	2.85	5.05	0.5 1								
372	7 UWC3 G1	2.87	5.34	0.5 3								
373	7 UWC3 G1	2.91	5.11	0.4 8								
		Average:	5.05	2SD:	0.33							
374	7-051	3.08	12.17	0.5 2	-12.21	24.68	0.3	0.006	2	51.48	47.95	0.0

375	7-052	3.12	12.95	0.4 9	-11.56	24.79	0.3	0.008	3	52.16	47.27	0.3
376	7-053	1.99	9.81	0.2 7	-5.32	15.21	0.3	0.001	NC			
377	7-054	2.79	14.44	0.5	-7.84	22.46	0.3	0.008	2	55.27	42.11	3.1
378	7-054a	1.85	15.6	0.4 3	-10.81	26.7	0.3	0.009	3	51.3	48.99	0.8
379	7-054b	2.74	13.13	0.3 9	-12.21	25.65	0.3	0.013	3	50.63	49.74	0.0
380	7-055	2.85	12.52	0.4 8	-12.21	25.03	0.3	0.007	4	50.19	50.04	0.0
381	7-070	2.76	15.81	0.5 5	-12.21	28.37	0.3	0.008	2	50.96	50.03	0.6
382	7 UWC3 G1	2.62	5.43	0.5 3								
383	7 UWC3 G1	2.62	5.4	0.5								
384	7 UWC3 G1	2.71	5.43	0.5 6								
385	7 UWC3 G1	2.8	5.23	0.4 9								
		Average:	5.27	2SD:	0.3							
386	7-073	3.14	13.47	0.3 5	-12.25	26.04	0.38	0.007	2	47.49	49.76	0.9
387	7-074	3.09	14.61	0.5 3	-12.25	27.18	0.38	0.007	2	50.75	48.8	0.1
388	7-075	3.09	14.56	0.4 5	-1.82	16.41	0.38	0.008	3	48.46	53.53	0.0
389	7-079	2.8	15.72	0.4 4	-2.2	17.96	0.38	0.005	Calcite	95.53	3.75	0.2
390	7-080	3.07	13.25	0.4 5	-12.25	25.82	0.38	0.008	3	52.44	47.75	0.3
391	7-081	3.01	13.53	0.5 1	-10.84	24.64	0.38	0.010	2	50.13	49.45	0.2

392	7-081a	3.08	14.5	0.4 9	-12.25	27.08	0.38	0.007	2	53.33	47.05	0.0
393	7-081b	2.15	8.3	0.3 2	-5.36	13.73	0.38	0.006	NC			
394	7-082	2.15	8.3	0.3 2	-5.36	13.73	0.38	0.004	NC			
395	7 UWC3 G1;	2.89	5.04	0.5 3								
396	7 UWC3 G1;	2.98	5.35	0.4 3								
397	7 UWC3 G1;	3.01	5.01	0.5 4								
398	7 UWC3 G1;	2.99	5.03	0.4 7								
		Average:	5.24	2SD:	0.38							
399	7-029	2.23	8.28	0.2 6	-5.61	13.97	0.36	0.001		52.97	46.78	0.0
400	7-030	3.14	12.81	0.4 5	-12.5	25.63	0.36	0.009	2	52.12	47.92	0.1
401	7-037	3.23	12.34	0.4 7	-12.5	25.15	0.36	0.006	2	50.16	49.93	0.2
402	7-037a	3.29	15.37	0.4	-11.84	27.54	0.36	0.007	2	53.05	46.55	0.4
403	7-038	3.24	12.51	0.6 3	-12.5	25.33	0.36	0.006	2	50.6	49.28	0.1
404	7-038a	3.33	14.59	0.5 1	-12.5	27.44	0.36	0.010	2	53.44	46.08	0.2
405	7-043	0.02	32.95	26. 24	NA	NA	NA	0.277	NC			
406	7-044	2.18	17.09	0.2 1	-5.61	22.83	0.36	0.002	NC			
407	7 UWC3 G1	3	4.73	0.4 8								

408	7 UWC3 G1	3.04	4.89	0.49								
409	7 UWC3 G1	3.04	4.89	0.57								
410	7 UWC3 G1	3.1	4.9	0.48								
		Average:	4.98	2SD:	0.36							
Sample Mount No. 6. 13 µm beam, 1.2 nA intensity. October 9th 2015												
411	6 UWC3 G1	2.75	5.16	0.44								
412	6 UWC3 G1	2.83	5.16	0.54								
413	6 UWC3 G1	2.87	5.13	0.48								
414	6 UWC3 G1	2.88	4.96	0.5								
415	6-004	2.12	8.21	0.26	-5.49	13.78	0.16	0.001	NC			
416	6-005	2.76	19.24	0.63	-12.38	32.02	0.16	0.005	Calcite	97.35	2.28	0.5
417	6-005a	3.05	16.42	0.41	-12.38	29.16	0.16	0.005	2	46.14	54.16	0.3
418	6-006	3.16	16.05	0.46	-12.38	28.78	0.16	0.005	2			
419	6-007	2.74	18.85	0.53	-12.38	31.62	0.16	0.002	4	44.92	51.46	3.5
420	6-009	2.83	19.19	0.55	-12.38	31.97	0.16	0.004	Calcite	97.41	2.32	0.4
421	6-010	2.83	19.19	0.55	-12.38	31.97	0.16	0.001	Calcite	96.3	3.06	0.3
422	6-027	0.01	-35.46	38.45	NA	NA	NA	0.213	Er			

423	6 UWC3 G1	2.83	5.01	0.5 2								
424	6 UWC3 G1	2.79	5.1	0.5 3								
425	6 UWC3 G1	2.79	5.2	0.5 8								
426	6 UWC3 G1	2.78	5.09	0.5 1								
427	6-027a	0.07	-1.13	8.4 9	NA	NA	NA	0.074	Er			
428	6-027b	2.33	19.17	0.5 4	NA	NA	NA	0.006	Er			
429	6-027c	0.03	-3.65	20. 26	NA	NA	NA	0.136	Er			
430	6-028	2.94	12.21	0.4 6			0.25	0.007	NF			
431	6-029	2.62	18.95	0.5 3	-12.42	31.77	0.25	0.007	Calcite			
432	6-030	2.67	19.48	0.5 5	-12.42	32.3	0.25	0.004	Calcite	97.3	2.61	0.4
433	6-031	2.59	19.49	0.6 4	-12.42	32.31	0.25	0.006	Calcite	98.08	1.73	0.0
434	6 UWC3 G1	2.72	5.16	0.5 4								
435	6 UWC3 G1	2.8	5.15	0.4 1								
436	6 UWC3 G1	2.96	4.81	0.4 7								
437	6 UWC3 G1	2.99	4.97	0.5 2								
		Average:	5.1	2SD:	0.16							

438	6-032	2.77	18.05	0.4 6	-12.53	30.97	0.3	0.004	Calcite	96.66	2.66	0.2
439	6-033	2.94	18.35	0.4 8	-12.53	31.27	0.3	0.004	Calcite	97.25	2.63	0.3
440	6-034	2.86	19.34	0.5 5	-12.53	32.27	0.3	0.007	Calcite	98.25	2.45	0.1
441	6-035	2.91	18.89	0.5 7	-12.53	31.81	0.3	0.004	Calcite	97.96	2.7	0.0
442	6-036	3.36	15.93	0.4 8	-9.76	25.94	0.3	0.002	3	42.99	54.48	2.1
443	6-037	3.27	12.93	0.4 8	-9.76	22.91	0.3	0.003	1	45.89	53.17	2.1
444	6-038	2.87	17.93	0.5 4	-12.53	30.84	0.3	0.004	Calcite	97.27	2.84	0.0
445	6-039	2.88	19.21	0.4 9	-12.53	32.14	0.3	0.005	Calcite	99.17	1.35	0.1
446	6 UWC3 G1	2.97	4.87	0.5								
447	6 UWC3 G1	2.96	4.88	0.4 8								
448	6 UWC3 G1	2.93	4.81	0.5 3								
		Average:	4.95	2SD:								
449	6-040	2.87	19.61	0.4 8	-12.42	32.44	0.43	0.002	Calcite	97.73	1.73	0.4
450	6-040a	3.27	15.7	0.4 4	-9.06	24.99	0.43	0.002	1	46.2	54.03	0.4
451	6-059	2.83	20.08	0.4 8	-12.42	32.91	0.43	0.002	Calcite	97.93	2.05	0.1
452	6-059a	2.82	19.4	0.6	-12.42	32.22	0.43	0.004	Calcite	99.09	1.33	0.0
453	6-059b	2.76	19.83	0.5 3	-12.42	32.66	0.43	0.005	Calcite	99.13	0.73	0.3
454	6-062	2.81	18.8	0.4 8	-12.42	31.62	0.43	0.005	Calcite	97.93	2.06	0.1

455	6-063	2.8	19.29	0.5 3	-12.42	32.11	0.43	0.007	Calcite	98.45	1.99	0.0
456	6-064	2.83	18.69	0.5 2	-12.42	31.51	0.43	0.002	Calcite	99.27	0.9	0.0
457	6 UWC3 G1	2.84	5.4	0.5 4								
458	6 UWC3 G1	2.85	5.08	0.5 2								
459	6 UWC3 G1	2.84	5.11	0.5 9								
460	6 UWC3 G1	2.85	5.24	0.4 9								
		Average:	5.06	2SD:	0.43							
461	6-074	2.75	19.25	0.5 7	-12.25	31.89	0.22	0.003	Calcite	97.51	2.48	0.0
462	6-075	2.75	19.47	0.5 5	-5.6	25.21	0.22	0.004	4	43.6	54.03	0.4
463	6-075	2.75	19.47	0.5 5	-5.6	25.21	0.22	0.004	Cal rep site number	97.05	2.19	0.0
464	6-077	2	15.64	0.3	-5.36	21.12	0.22	0.001	NC			
465	6-077a	1.99	15.96	0.3	-5.36	21.44	0.22	0.001	NC			
466	6-077b	2.07	8.37	0.2 7	-5.36	13.81	0.22	0.001	NC			
467	6-077c	2.06	8.66	0.3	-5.36	14.1	0.22	0.001	NC			
468	6-070	2.71	19.5	0.5			0.22	0.004	Er			
469	6-071	3.18	16.61	0.3 7	-12.25	29.22	0.22	0.002	Calcite	97.3	2.46	0.2
470	6-068	2.85	15.57	0.3 4	-12.25	28.17	0.22	0.006		42	58.55	0.0
471	6 UWC3 G1	2.78	5.23	0.4 9								

472	6 UWC3 G1	2.77	5.35	0.4 9								
473	6 UWC3 G1	2.76	5.17	0.5 4								
474	6 UWC3 G1	2.75	5.28	0.4 9								
		Average:	5.23	2SD:	0.22							
Sample Mount No. 1. 13 µm beam, 1.2 nA intensity. October 9th 2015												
475	1 UWC3 G1	2.98	5.29	0.5 3								
476	1 UWC3 G1	2.84	5.27	0.4 7								
477	1 UWC3 G1	2.78	5.19	0.5								
478	1 UWC3 G1	2.72	5.05	0.5 6								
479	1-084	2.8	13.06	0.6	-12.35	25.72	0.2	0.007	2	49.57	51.37	0.0
480	1-084a	2.88	14.37	0.6 4	-11.69	26.37	0.2	0.008	2	49.45	50.75	0.0
481	1-085	2.84	12.7	0.5 2	-12.35	25.35	0.2	0.008	2	50.05	49.94	0.0
482	1-101	2.76	13.95	0.5 8	-12.35	26.62	0.2	0.009	4	49.45	50.75	0.7
483	1-102	2.76	12.63	0.4 2	-12.35	25.29	0.2	0.005	4	47.69	56.15	1.4
484	1-103	2.81	13.7	0.5	-12.35	26.37	0.2	0.008	4	50.69	50.53	0.2
485	1-104	2.78	14.16	0.4 9			0.2	0.007	Er			
486	1-105	2.99	14.47	0.4	-12.39	27.2	0.16	0.005	4	48.66	52.15	0.0
487	1-106	2.96	13.04	0.4 4	-12.39	25.74	0.16	0.008	4	48.85	50.37	1.0
488	1-107	2.95	12.36	0.5 7	-12.39	25.06	0.16	0.006	4	47.98	52.14	0.2

489	1-108	2.93	13.37	0.4 4	-12.39	26.08	0.16	0.007	2	49.88	54.21	0.2
490	1-109	2.93	12.97	0.4 6	-12.39	25.68	0.16	0.011	2	45.84	54.92	1.3
491	1-110	2.89	13.61	0.4 8	-12.39	26.32	0.16	0.008	3	47.54	52.23	0.0
492	1-111	2.01	14.2	0.2 1	-5.5	19.81	0.16	0.001	NC			
493	1-112	2.88	12.22	0.4 8			0.16	0.006	Er			
494	1-113	2.84	13.6	0.3 8	-12.39	26.31	0.16	0.005	2	48.17	52	0.0
495	1 UWC3 G1	2.73	5.2	0.5 1								
496	1 UWC3 G1	2.66	5.12	0.7 5								
497	1 UWC3 G1	2.7	5.19	0.4 6								
498	1 UWC3 G1	2.9	4.94	0.4 8								
		Average:	5.16	2SD:	0.23							
499	1-114	3.19	12.61	0.4 6			0.41	0.006	Er			
500	1-115	3.18	11.83	0.6 4			0.41	0.016	Er			
501	1-116	3.15	14.19	0.4 4			0.41	0.007	Er			
502	1-117	3.09	14.58	0.2 5			0.41	0.013	Er			
503	1-118	3.22	11.11	0.6 6			0.41	0.021	Er			
504	1-119	3.13	12.53	0.4 5			0.41	0.007	Er			

505	1-120	3.17	11.81	0.55			0.41	0.008	Er			
506	1-121	3.1	14.38	0.59			0.41	0.007	Er			
507	1-122	3.13	13.47	0.5			0.41	0.006	Er			
508	1 UWC3 G1	3.02	4.73	0.49								
509	1 UWC3 G1	2.99	4.97	0.56								
510	1 UWC3 G1	2.99	4.64	0.51								
511	1 UWC3 G1	2.96	4.97	0.54								
		Average:	4.97	2SD:	0.41							
Sample Mount No. 5. 13 µm beam, 1.2 nA intensity. October 9th 2015												
512	5 UWC3 G2	3.04	4.92	0.52								
513	5 UWC3 G2	3.01	5.11	0.5								
514	5 UWC3 G2	3	4.94	0.5								
515	5 UWC3 G2	2.97	5.08	0.52								
516	5-072	3.21	15.35	0.37	-12.49	28.19	0.16	0.003	2	49.75	50.2	0.0
517	5-101	2.09	10.6	0.38	-5.6	16.3	0.16	0.001	NC			
518	5-102	2.99	11.28	0.53	-11.98	23.55	0.16	0.008	2	52.3	47.7	0.0
519	5-103	3.06	13.83	0.45	-12.13	26.28	0.16	0.006	3	50.1	49.9	0.0
520	5-104	2.14	5.23	0.28	-5.6	10.89	0.16	0.001	NC			

521	5-105	2.08	3.69	0.2 8	-5.6	9.35	0.16	0.008	NC			
522	5-106	2.13	5.87	0.2 5	-5.6	11.54	0.16	0.001	NC			
523	5-107	2.94	14.7	0.5 4	-12.49	27.54	0.16	0.003	4	50.85	49.1	0.3
524	5 UWC3 G2	2.91	4.9	0.4 9								
525	5 UWC3 G2	2.91	4.99	0.4 7								
526	5 UWC3 G2	2.88	4.93	0.4 5								
527	5 UWC3 G2	2.89	5.03	0.4 3								
		Average:	4.99	2SD:	0.16							
528	5-108	2.86	14.6	0.3 5	-12.29	27.22	0.14	0.004	6	51.51	48.03	0.3
529	5-109	3.15	17.58	0.4	-12.48	30.44	0.14	0.001	6	50.8	46.54	6.9
530	5-110	2.08	5.64	0.2 3	-5.63	11.34	0.14	0.001	NC			
531	5-111	2.08	5.56	0.2 5	-5.63	11.26	0.14	0.001	NC			
532	5-112	2.08	5.8	0.2 7	-5.63	11.5	0.14	0.001	NC			
533	5-113	3.05	15.47	0.4 7	-12.52	28.35	0.14	0.002	2	52.16	44.41	3.2
534	5-114	3.01	18.42	0.3 7	-12.52	31.34	0.14	0.005	3	50.43	50.01	0.3
535	5-115	2.97	14.19	0.4 2	-12.52	27.05	0.14	0.002	4	52.3	47.98	0.1
536	5 UWC3 G2	2.82	5.01	0.4 5								

537	5 UWC3 G2	2.82	4.82	0.5 3								
538	5 UWC3 G2	2.82	4.97	0.5 8								
539	5 UWC3 G2	2.81	5.02	0.4 1								
		Average:	4.96	2SD:	0.14							
540	5-116	2.04	6.99	0.2 6	-5.63	12.7	0.14	0.001	NC			
541	5-117	2.96	13.78	0.5 5	-12.52	26.63	0.14	0.001	4	51.29	48.6	0.1
542	5-118	2.92	12.88	0.4 1	-12.52	25.73	0.14	0.003	4	51.06	49.43	0.5
543	5-119	1.96	8.79	0.2	-5.63	14.5	0.14	0.001	NC			
544	5-120	1.94	9.77	0.2 6	-5.63	15.49	0.14	0.001	NC			
545	5-121	1.93	9.88	0.2 7	-5.63	15.6	0.14	0.001	NC			
546	5-122	2.83	12.4	0.3 9	-12.52	25.23	0.14	0.003	2	50.52	49.59	0.4

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Pit Analysis

After ion microprobe analysis a combination of Scanning Electron (SE), Back Scattered (BSE) microscopy and Wavelength Dispersive Spectroscopy (SEM-WDS) was used to relocate and characterise each individual pit. Pits with an irregular morphology were excluded. In this study ‘pit irregularity’ is defined as and includes pits which are positioned on cracks, spots which break into crystals and/or inclusions other than the target mineral and spots which overlap pores and vugs. Analyses which were not of calcite or dolomite were also excluded. Analyses were also excluded where the pit could not be found or the pit identity confirmed. An explanation each excluded analysis is given in Table X. In total 111 measurements were excluded from a total of 308 analyses

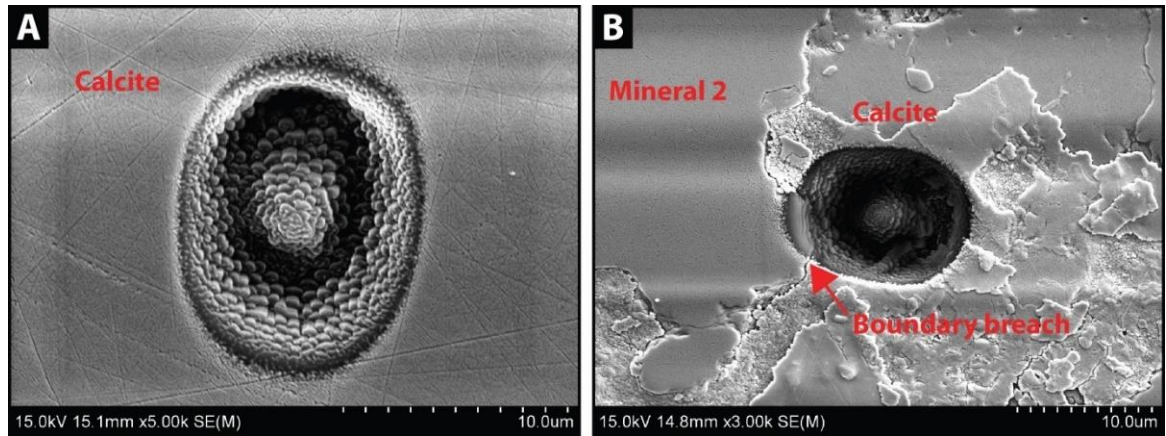


Figure X - Examples of SIMS pits a) Regular pit, positioned in the centre of a calcite crystal in sample 2-55B; note the ellipsoidal shape and size. Note, the pit is shown rotated 90° to the orientation it was created in; b) Irregular pit positioned at the edge of calcite cement, breaking into a second mineral (mineral 2), contaminating the ablated sample, in sample 2-55B.

1013 **Table X** – Details of pits excluded from further interpretations. Not found = where the pit couldn't be located for integrity checking. Other Mineral = analyses of minerals
1014 other than calcite or dolomite and were commonly feldspar or quartz. Error = Refers to low count rates obtained by the detector.

Analysis ID	Explanation	Analysis ID	Explanation	Analysis ID	Explanation	Analysis ID	Explanation
1-051b	Irregularity	2-032	Not Found	3-084	Other Mineral	6-075	Not Found
1-052	Error	2-034	Not Found	3-084a	Other Mineral	6-077	Other Mineral
1-054	Not Found	2-035	Not Found	3-085	Other Mineral	3-086	Not Found
1-067g	Not Found	2-036	Not Found	4-008	Other Mineral	3-092	Other Mineral
1-073	Irregularity	2-038	Not Found	4-011	Irregularity	6-077a	Other Mineral
1-075	Irregularity	2-041	Not Found	4-038	Other Mineral	6-077b	Other Mineral
1-084a	Not Found	2-043	Not Found	4-043	Irregularity	6-077c	Other Mineral
1-104	Error	2-045	Not Found	4-066	Not Found	7-006	Other Mineral
1-111	Other Mineral	2-048	Irregularity	4-069	Other Mineral	7-020	Other Mineral
1-112	Error	2-061	Other Mineral	4-086	Other Mineral	7-021	Other Mineral
1-114	Error	3-006	Other Mineral	4-100	Other Mineral	7-023	Other Mineral
1-115	Error	3-011	Other Mineral	5-005	Other Mineral	7-024	Other Mineral
1-116	Error	3-012	Other Mineral	5-028	Other Mineral	7-029	Irregularity
2-005	Not Found	3-017	Irregularity	5-028a	Other Mineral	7-040	Other Mineral
2-007	Other Mineral	3-025	Irregularity	5-028b	Other Mineral	7-041a	Other Mineral
2-008	Not Found	3-029	Other Mineral	5-053	Other Mineral	7-043	Other Mineral
2-009	Irregularity	3-030	Other Mineral	5-082	Other Mineral	7-044	Other Mineral
2-009-2	Other Mineral	3-031	Other Mineral	5-084	Error	7-048	Irregularity
2-009-3	Other Mineral	3-033	Not Found	5-089	Other Mineral	7-051	Irregularity
2-013	Not Found	3-034	Not Found	6-004	Other Mineral	7-053	Other Mineral
2-018	Other Mineral	3-035	Other Mineral	6-006	Not Found	7-060	Other Mineral
2-021	Other Mineral	3-036	Not Found	6-027	Error	7-075	Irregularity
2-022	Not Found	3-037	Not Found	6-027a	Error	7-079	Not Found
2-022b	Not Found	3-038	Not Found	6-027b	Error	7-081b	Other Mineral
2-027	Not Found	3-039	Not Found	6-027c	Error	7-082	Other Mineral
2-028a	Other Mineral	3-040	Not Found	6-028	NC	7-098	Other Mineral
2-030	Not Found	3-041	Irregularity	6-068	Irregularity	7-098	Other Mineral
2-031	Not Found	3-081	Error	6-070	Error		

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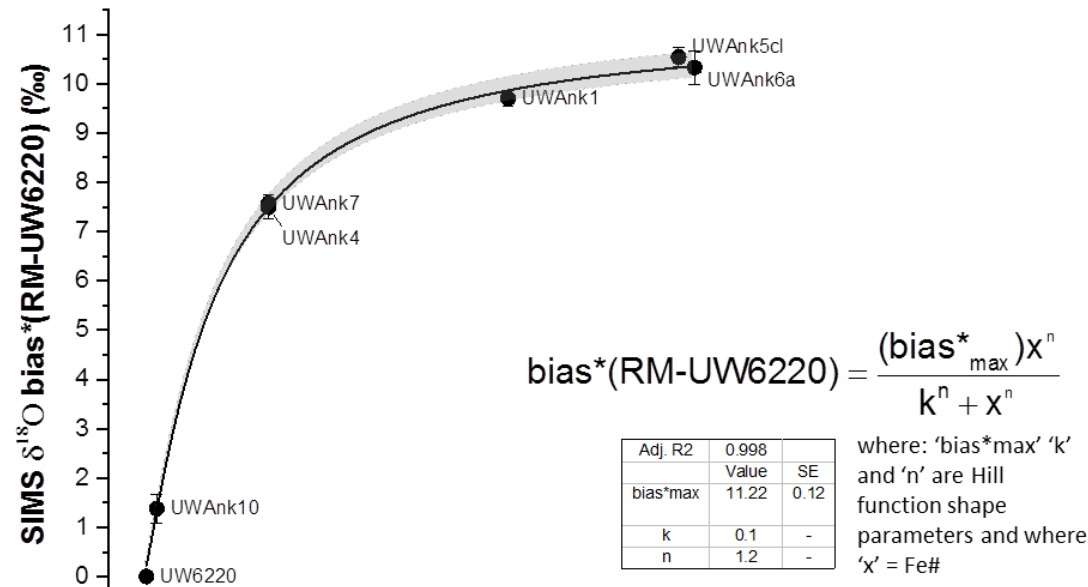
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Iron Correction

1019 (a) Plot relating the SIMS $\delta^{18}\text{O}$ bias (‰) to the cation composition of the dolomite–ankerite solid solution series [$\text{Fe\#} = \text{Fe}/(\text{Mg}+\text{Fe})$] for a
1020 typical calibration using a 10 μm diameter spot size. The sample matrix effect can be accurately estimated using the Hill equation, which is
1021 commonly employed to describe relations of ‘concentration’ versus ‘measured effect’ type, especially in systems that behave non-linearly and
1022 reach saturation. (b) Plot of the calibration residual. For most reference materials in the suite, the averaged measured value of $\delta^{18}\text{O}$
1023 bias*(RMUW6220) differs by < 0.3‰ from the value predicted by the calibration (depicted by solid lines). Modified from Sliwinski et al., (2015).
1024 Figure from Orland et al., pers. com. (2015).

M.Brodie Session 2015.Oct.5 (10 µm spot-size)

a.



b.

